ISOBARIC VAPOUR-LIQUID EQUILIBRIUM STUDIES OF DICHLOROMETHANE-METHANOL AND METHANOL-2- BUTANOL SYSTEMS

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
SRIMANNARAYANA MURTHY, K.

to the

DEPARTMENT OF CHEMICAL ENGINEERING

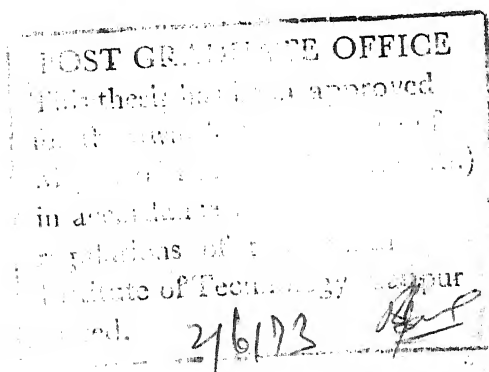INDIAN INSTITUTE OF TECHNOLOGY KANPUR
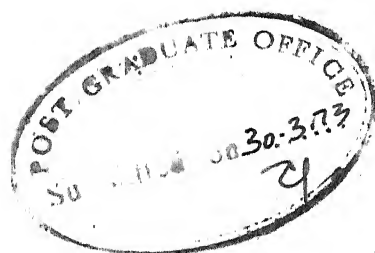
MARCH 1973

CERTIFICATE

It is certified that this work has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

March 30, 1973

Arvind P. Kudchadker
Associate Professor
Department of Chemical Engineering
Indian Institute of Technology
Kanpur, India

<u>ACKNOWLEDGEMENTS</u>

TABLE OF CONTENTS

....

LIST OF FIGURES

....

LIST OF TABLES

....

ABSTRACT

The isobaric vapor-liquid equilibrium data for the systems dichloromethane-methanol and methanol-2-butanol have been investigated at 760 mm Hg. An improved vapor recirculating type of equilibrium still has been used for this purpose.

The dichloromethane-methanol system exhibited a minimum boiling azeotrope at 37.4°C and 0.84 mole fraction of dichloromethane. The activity coefficients for this system have been calculated taking the vapor phase non-ideality into consideration. It was observed that the activity coefficient of dichloromethane exhibited a maxima at a low concentration range of (about 0.06) dichloromethane but no minima was observed in the activity coefficient of methanol. This peculiar phenomena seems to be typical of chloromethane-alcohol systems.

The methanol-2-butanol system did not exhibit an azeotrope and is almost ideal because the actual magnitudes of the activity coefficients for both the components are nearer to unity in most of the composition range. The activity coefficients were calculated assuming ideal behavior in the vapor phase ($\emptyset=1$) in the absence of second virial coefficient data in the temperature range of investigation. The experimental data for both the systems were not consistent according to the Herrington's test. Unless the enthalpy of mixing data are available, it is difficult to conclude about the consistency of the data. The activity coefficients are estimated to be accurate upto $\pm$ 0.01.

The excess liquid molar volumes for both the binary systems were measured at $25 \pm .01°C$ using a modified Robertson pycnometer. Both the systems were found to exhibit positive deviations from ideality. The density measurements are estimated to be accurate upto $\pm .0005$ gms/cm^3. Thus the excess molar volumes of mixing are accurate to $\pm$ 0.1 cm^3/gm.mole.

...

NOMENCLATURE

A	Constant of the Antoine equation.
B	Constant of the Antoine equation
B_{ij}	Cross virial coefficient of components i and j
C	Constant of the Antoine equation.
°C	Degree Celsius
E.M.F.	Electromotive force
f	Fugacity
G	Gibbs energy
H	Enthalpy
h^E	Excess enthalpy per mole
Hg	Mercury
i	Species 'i'
j	Species 'K'
°K	Degree Kelvin
l	liquid phase
n	Number of components
n_D	Refractive Index
n_i	Number of moles of component 'i'
n_T	Total number of moles
P_c	Critical pressure
P_S	Saturated vapor pressure
p	Partial pressure
R	Gas Constant
T	Absolute temperature
T_c	Critical temperature

t	Celsius temperature
V	Total volume
v	Vapor phase
v_i^l	Liquid molar volume
v^E	Excess molar volume
x	liquid phase mole fraction
y	Vapor phase mole fraction
Z	Compressibility factor
Z_c	Critical compressibility factor
π	Total number of phases
ϕ	Fugacity coefficient
γ	Activity coefficient
μ	Chemical potential
μ'	Dipole moment
Σ	Summation sign
δ	Change in the variable.

CHAPTER I

INTRODUCTION

There are relatively few systems whose equilibrium relationships can be calculated from Rault's law and Dalton's law, i.e. from the known dependence of the vapor pressures of pure components on temperature. On the other hand there are a large number of important systems whose equilibrium relationships cannot be predicted from purely theoretical considerations and which must be obtained by a direct experimental determination.

The interaction of the constituent molecules both in the liquid and the vapor phases contribute to the non-ideality of the system. At conditions well removed from the critical region i.e. at low and moderate densities, the non-ideality in the liquid phase is always the dominant one compared to the non-ideality in the vapor phase. This is because, in the latter phase, the molecules are relatively far apart for them to interact with each other. However, the non-ideality in the vapor phase cannot altogether be neglected as had been clearly shown by Prausnitz(16). Its contribution is nevertheless significant.

The non-ideality in the liquid phase arises because of the difference in size and polarity of the constituent molecules and also due to the hydrogen bonding effects.

In the present study an attempt has been made to investigate the extent of non-ideality introduced when molecules of different polarities are considered. The two such systems chosen for study are:

1. Dichloromethane (μ = 1.56 D) - Methanol (μ' = 1.66 D) and

2. Methanol (μ' = 1.66 D) and 2-butanol (μ = 1.60D).

Sarma (19) and Chhotray (3) have studied the equilibrium properties of dichloromethane-methanol system at 760 mm Hg and 550 mm Hg pressures respectively. Curiously enough, at both the pressures the activity coefficient γ_1 of dichloromethane showed a maxima, while the activity coefficient γ_2 of methanol did not show a minima. This behavior does not satisfy the Gibbs-Duhem equation at constant temperature and pressure. According to the Gibbs-Duhem Equation,

$$x_1 \left. \frac{d \ln \gamma_1}{dx_1} \right|_{T,P} = - x_2 \left. \frac{d \ln \gamma_2}{dx_1} \right|_{T,P} \qquad (1.1)$$

if $\ln \gamma_1$ vs x_1 goes through a maximum, then $\ln \gamma_2$ vs x_1 should go through a minimum. However the above results of Sarma and Chhotray were at isobaric conditions only and as such the deductions from Eqn.(1.1) do not strictly apply.

The following were the azeotropic compositions and the

corresponding minimum boiling temperatures at 760, 750, and 550 mm Hg pressures as reported by Sarma (19), Tenn and Missen (21) and Chhotray (3), respectively.

1. At 760 mm Hg : x_1 = 0.805; t = 38.8°C

2. At 750 mm Hg : x_1 = 0.846; t = 37.2°C

3. At 550 mm Hg : x_1 = 0.885; t = 28.9°C

where,

x_1 = mole fraction of dichloromethane

t = minimum boiling temperature in degrees celcius (azeotropic temperature).

The above data show a big change in composition from x_1 = 0.805 to 0.846 for a small change in temperature of 1.6°C as compared to the change from 0.846 to 0.885 for a change in temperature of 8.3°C. This is intriguing and is quite unlikely.

The inconsistencies in the data at 760 mm Hg pressure could be attributed to the presence of some water (Sarma used analar grade methanol of 99.5 mole % purity, which contained some water) which would form complexes through hydrogen bonding in addition to dipole-dipole and higher order interactions with methanol and dichloromethane. Hence it was decided to repeat the dichloromethane - methanol system at 760 mm Hg pressure, using absolute methanol.

As a further part of our investigation, it was also decided to study some additional properties of these binary

systems which could throw some light on the peculiar behavior exhibited by the methanol-dichloromethane system (maxima in the activity coefficient in the dilute region of dichloromethane). It would be desirable to isolate if possible the contributions due to hydrogen bonding in the methanol molecule and the dipole-dipole interactions between methanol and dichloromethane molecules. It was felt that the infrared studies could tell us something about this problem through the band shifts as a function of concentration of dichloromethane. These studies are being carried out by other investigators here.

For the present study it was decided to measure excess molar volumes at 25°C at various concentrations hoping that this would give answers to some of the questions relating to the activity coefficients of dichloromethane-methanol system.

***

CHAPTER II

THEORY OF VAPOR-LIQUID EQUILIBRIA

An equilibrium state is the one from which there
is no tendency for it to depart spontaneously. It had
been well established by Gibbs (16) that a liquid phase
and a vapor phase are said to be in thermodynamic equili-
brium when at constant temperature and pressure, the
"Chemical Potential" μ_i, of each molecular species
present is the same in both the phases as shown below.
These identities hold for a system of m components and π
phases at constant temperature and pressure.

$$\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} = \ldots\ldots\ldots \mu_1^{(\pi)}$$

$$\mu_2^{(1)} = \mu_2^{(2)} = \mu_2^{(3)} = \ldots\ldots\ldots \mu_2^{(\pi)} \quad (2.1)$$

$$\mu_m^{(1)} = \mu_m^{(2)} = \mu_m^{(3)} = \ldots\ldots\ldots \mu_m^{(\pi)}$$

The superscript in the parentheses denotes the phase,
and subscript denotes the species.

Though chemical potential is conceived as a driving
force for mass transfer across a phase boundary, it does
not in itself provide an insight to describe quantitatively
the distribution at equilibrium of every component among
all the species present. To facilitate this, it was
Lewis(16) who related the chemical potential to a less

abstract quantity, fugacity f, having the units of pressure, by the following relationship:

$$\mu_i = \mu_i^O + RT \ln f_i \qquad (2.2)$$

where μ_i^O is the chemical potential in the reference state.

From Eqns. (2.1) and (2.2) it follows that

$$f_i^v = f_i^l \qquad (2.3)$$

where v and l refer to the vapor and liquid phases respectively.

The desired relationship between the fugacity and the experimentally accessible quantities temperature T, pressure P, and composition is obtained by defining two auxiliary functions - namely, the fugacity coefficient $\emptyset$, and the activity coefficient γ. The relationships are:

$$\emptyset_i \equiv \frac{f_i^v}{y_i P} \qquad (2.4)$$

and

$$\gamma_i \equiv \frac{f_i^l}{x_i f_i^{ol}} \qquad (2.5)$$

where,

P = total pressure of the system, and

f_i^{ol} = standard state liquid fugacity of component i.
In Eqns (2.4) and (2.5) y_i and x_i are the mole fractions in the liquid and the vapor phases, respectively.

From Eqns. (2.3), (2.4) and (2.5) it follows that

$$\emptyset_i y_i P = \gamma_i x_i f_i^{ol} \qquad (2.6)$$

This is the key Equation for calculating any thermo-
dynamic equilibrium property and is pertinent to the present
study (16).

Analyzing $\emptyset_i$ and γ_i for their physical significance,
the fugacity coefficient, $\emptyset_i$, can be viewed as a measure of
non-ideality in the vapor phase arising due to the attractive
and repulsive forces between the molecules. The activity
coefficient γ_i is the non-ideal correction term in the
liquid phase arising due to the unlike interaction of the
constituent molecules because of their difference in mole-
cular size, polarity, and hydrogen bonding, etc.

Having defined $\emptyset_i$ and γ_i, a brief outline is given
here as to the method of their calculation from the experi-
mentally measured quantities.

The fugacity coefficient is a function of temperature,
total pressure and composition of the vapor phase and it can
be obtained by the following thermodynamic relation (1).

$$\ln \emptyset_i = \frac{1}{RT} \int_V^{\infty} \left(\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right) dV - \ln Z \qquad (2.7)$$

$$j \neq i$$

where Z is the compressibility factor of the vapor mixture,

$$Z = \frac{PV}{(n_1 + n_2 + \text{----})RT} \qquad (2.8)$$

Though in principle any equation of state can be
employed in Eqn.(2.7), virial equation of state is chosen
because of its firm theoretical basis. Virial equation

expressed as a power series in reciprocal molar volume($1/v$), is

$$Z = \frac{Pv}{RT} = 1 + \frac{B_v(T)}{v} + \frac{C_v(T)}{v^2} + \text{------} \qquad (2.9)$$

where B_v is the second virial coefficient which accounts for interactions between pairs of molecules, C_v is the third virial coefficient which accounts for interactions of triplets of molecules, and, so on. At low pressures, third and higher order interactions are small and hence Eqn.(2.9) is truncated upto the second virial coefficient and used for further calculations.

$$Z = \frac{Pv}{RT} = 1 + \frac{B_v(T)}{v} \qquad (2.10)$$

For a pure vapor, the virial coefficients are functions only of temperature, for a mixture they are also functions of composition as given by the rigorous relationship:

$$B_{v\ mix} = \sum_i^N \sum_j^N y_i y_j B_{v\ ij} \qquad (2.11)$$

Substituting Eqns. (2.8), (2.10) and (2.11) into Eqn. (2.7), we get

$$\ln \phi_i = \frac{2}{V_{mix}} \left(\sum_j^N y_j B_{v\ ij} \right) - \ln Z_{mix} \qquad (2.12)$$

and Z and v are related by

$$Z = 1 + \frac{\sum_i^N \sum_j^N y_i y_j B_{v\ ij}}{v} \qquad (2.13)$$

For obtaining reliable values of B_{ii} and B_{ij}, it is necessary to have accurate volumetric data both for pure

gases and mixtures, in the absence of which they have to be predicted. Out of the various models proposed for the prediction, the three parameter model based on the principle of corresponding states proposed by Pitzer and Curl (15) was used in the present calculations.

The reference state fugacity for a condensable component is given by,

$$f_i^{ol} = P_i^s \, \phi_i^s \, \exp \int_{P_i^s}^{0} \frac{v_i^l}{RT} \, dP \qquad (2.14)$$

where

P_i^s = saturation vapor pressure of pure liquid i at temperature T,

ϕ_i^s = fugacity coefficient of pure saturated vapor at temperature T and pressure P_i^s,

and v_i^l = molar volume of pure liquid i at temperature T.

ϕ_i^s in Eqn.(2.14) can be calculated from Eqn.(2.12) by replacing j by i.

Once the equilibrium values of temperature, pressure and composition are known, the fugacity coefficient ϕ_i and the reference state fugacity f_i^{ol} are calculated by the above method. Then the activity coefficient γ_i is calculated using Eqn.(2.6).

After obtaining the activity coefficients, one can derive the excess properties like excess enthalpy, excess Gibbs energy and other thermodynamic excess properties by using appropriate models (16).

CHAPTER III

EXPERIMENTAL SET-UP

The rational design and operation of equilibrium stage separation processes, such as distillation columns, demand the need for accurate vapor-liquid equilibrium data and this has given rise to large number of equilibrium stills (5). Whatever may be the type of the still used, the principle involved is the separation of the feed of known composition into its true equilibrium vapor and liquid phases.

Basically, the vapor-liquid equilibrium data can be obtained by either static or dynamic methods. Static methods by and large yield exceptionally accurate results but are quite tedious and are not in common use at low and medium pressure ranges. This is because the analysis of gas and liquid samples poses certain difficulties.

Of the dynamic methods, vapor recirculating still is a better design than the liquid recirculating type, from the theoretical stand point (8). The still used in the present investigation is the vapor recirculating type, a modified design of Hipkin and Myers proposed by Lodl and Scheller (20) and is shown in Fig. 1.

The still is made of pyrex glass to withstant pressures as high as 3-4 atmospheres and temperatures as high as 500°-600°C. It consists of four cylindrical glass pipes
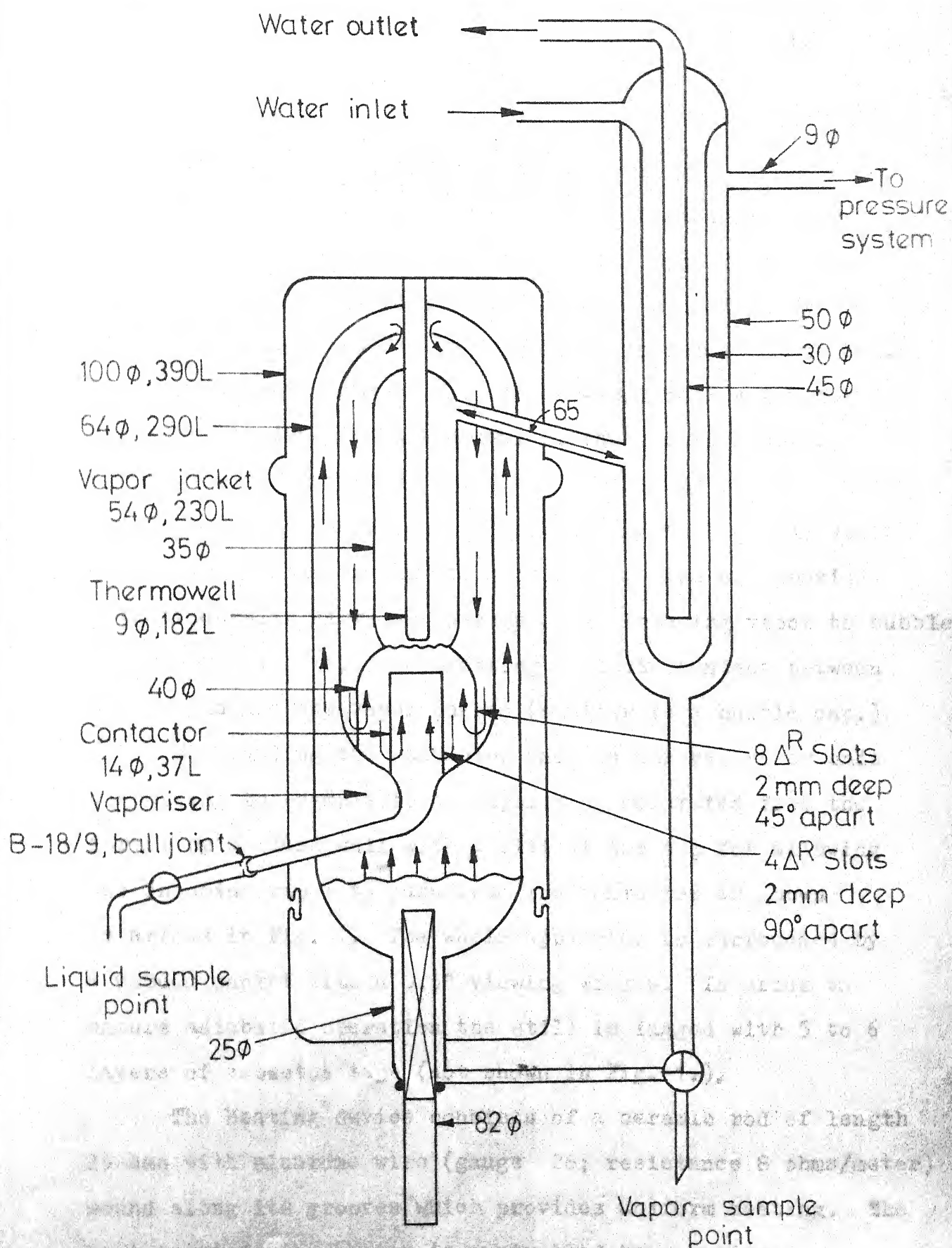
Fig. 1–Equilibrium cell and condenser assembly.
(All dimensions in mm)

connected to each other by careful annealing.

The contactor unit consists of a thermowell (for a thermocouple) extending right from the top of the still and the contactor (open at both ends) is placed below the well. The bottom end of the contactor is connected to a two way high vacuum stopcock through a B-18/9 ball joint for charging the feed and withdrawal of the liquid sample. The ball joint has been provided to avoid any strains on the tube connecting the still while operating the two way stopcock. The contactor and its surrounding tube are provided with triangular slots which enable the incoming vapor to bubble through the liquid, thus creating intimate contact between the liquid and the vapor phases (similar to a bubble cap.).

Surrounding the contactor unit is the vaporizer unit containing the sample to be vaporized, separated from the former by a glass wall with a slit at the top for allowing the incoming vapor to pass into the contactor as shown by arrows in Fig. 1. The whole apparatus is surrounded by a vacuum jacket with a 0.5" viewing window. In order to ensure adiabatic operation the still is lagged with 5 to 6 layers of asbestos tape (not shown in Fig. 1.).

The heating device consists of a ceramic rod of length 25 cms with nichrome wire (gauge 28; resistance 8 ohms/meter) wound along its grooves which provides uniform heating. The heat input to the heater is controlled by a variac.

The condenser used is essentially a shell and tube type with vapor condensing on the shell side and the cold water recirculating from a storage tank through a 'Tullu' water pump, on the tube side. The circulating water was always maintained below 25°C by adding ice to the storage tank frequently. Connecting the condenser and vaporizer unit of the still is a three way high vacuum stopcock, which is provided for the recirculation of the condensing vapor and for the withdrawal of the vapor sample from the condenser side.

A schematic line diagram of the experimental set-up is shown in Fig. 3.

A U-tube manometer was used (length 1.25 cms, dia 8 mm) with one end evacuated to a vacuum of the order of 10^{-3} to 10^{-4} mm Hg pressure and the other end connected to the system through a two way high vacuum stopcock. The manometric liquid used was triple distilled mercury and one could safely read any pressure between 0 to 760 mm Hg with an accuracy of 0.5 mm.

For the accurate measurement of pressure in the system, a two stage Swietoslawsky ebulliometer (5) was employed the details of which are shown in Fig.2. This permitted the simultaneous measurement of boiling and condensation temperatures as a criterion for the purity of the substance involved.
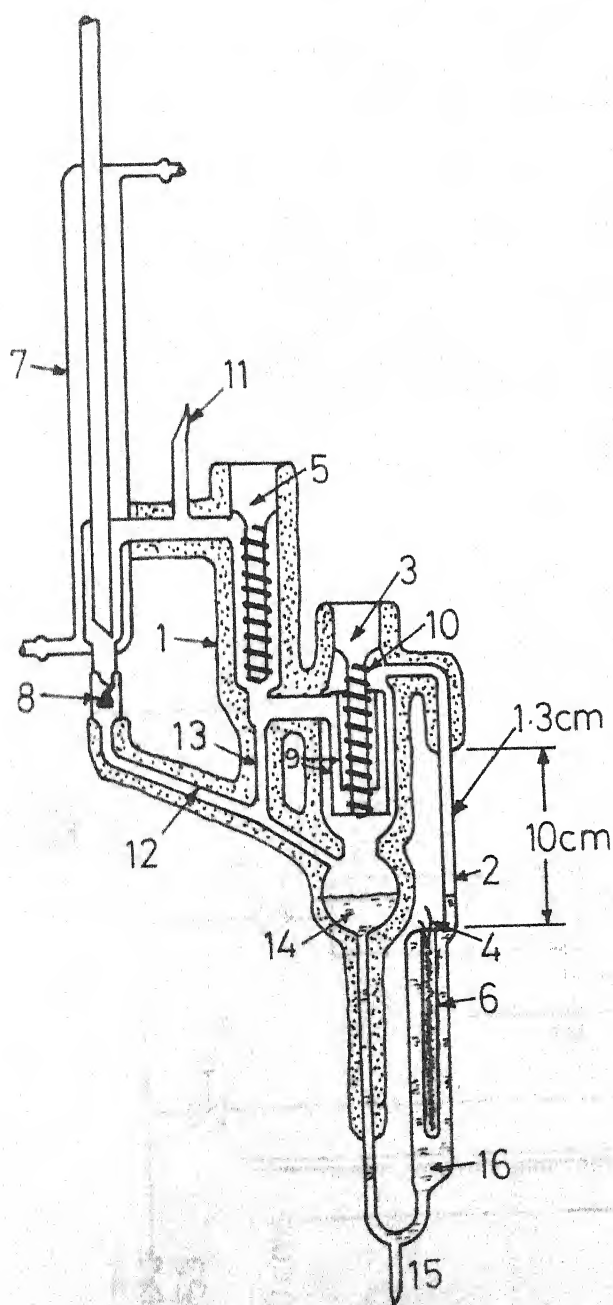
1   Asbestos insulation

2   Percolator tube

3   Boiling temp. well

4   Electrical heater

5   Condensation temp. well

6   Glass thread

7   Condenser

8   Drop counter

9   Glass shield (baffle)

10   Glass spiral

11   Sample seal-off

12   Condensate return tube

13   Condensate return tube

14   Reservoir

15   Sample take-off

16   Boiler

Fig. 2 – Differential Ebulliometer.
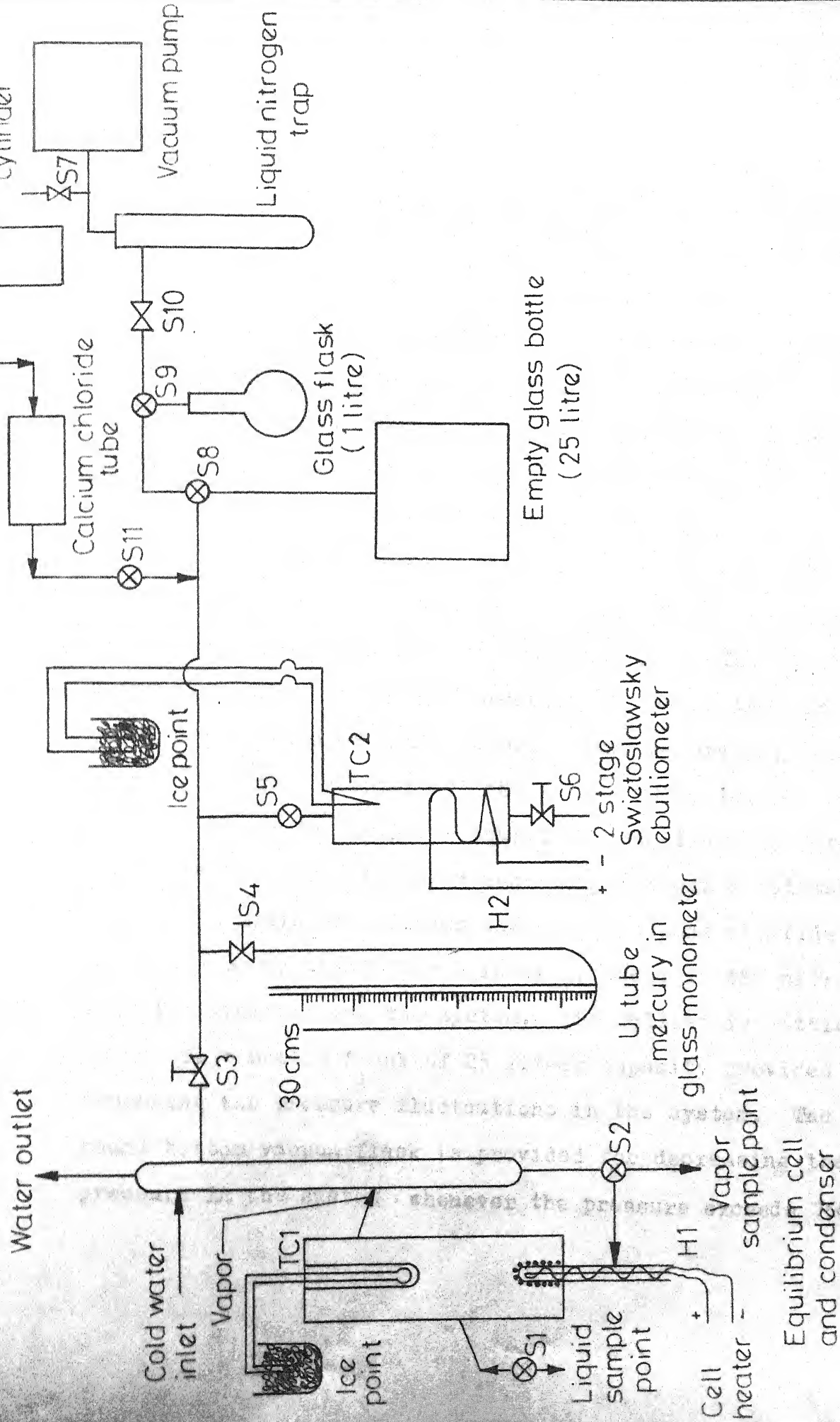
Fig. 3 – Schematic line diagram for the experimental set-up.

The ebulliometer consists of a boiler and condenser sections provided with thermowells for measuring boiling and condensing temperatures. The liquid in the boiler is heated by means of an electric heater (gauge -28, resistance 8 ohms/meter, and length - 5 meters), the heat input to which is controlled by a variac. The pure liquid vapor generated in the percolator tube enters the boiling temperature well, 3, where a part of it is condensed along the thermowell. The uncondensed vapor is led to the condensation temperature vessel, 5, where again part of it is condensed and returned to the reservoir through the return tube, 13. The final condensed vapors go to the condenser, 7, where they are completely condensed and returned to the reservoir, 14, through the drop counter and the return tube, 12.

As shown in Fig.3 the equilibrium cell and the ebulliometer are connected to the vacuum pump through a ballast and to the nitrogen cylinder through a calcium chloride packing tube to absorb any moisture present in the nitrogen used for pressurizing the system. The ballast is a thick-walled flat bottom flask of 25 liters capacity provided for dampening the pressure fluctuations in the system. The round bottom vacuum flask is provided for decreasing the pressure in the system whenever the pressure exceeds 760 mm Hg.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The operational procedure involved in obtaining the equilibrium data are described under the following headings:

1. Source and purity of the samples.

2. Feeding the sample into the equilibrium still.

3. Operation of the equilibrium still.

4. Measurement of equilibrium pressure and temperature.

5. Analysis of equilibrium liquid and vapor samples.

1. Source and Purity of the Samples:

A. **Dichloromethane:** Analar grade dichloromethane was supplied by Merck Company, Germany with a stated purity of 99.5 mole% or better. It was used without further purification.

B. **Methanol:** 99.5 mole% methanol supplied by British Drug House, India was distilled to obtain absolute methanol according to the procedure suggested by Vogel (24) and this sample was used in the present investigation.

C. **2-Butanol:** Analar grade 2-butanol with a stated purity of 99.5 mole% was supplied by Reanal Company, Hungary and it was also used without further purification.

The experimentally determined normal boiling point, refractive index and density of each sample is compared with the "best" literature (25) values in Appendix III.

2. Feeding the Sample into the Equilibrium Still:

Stopcocks S1, S2 and S6 were closed and the rest of them were kept open to the vacuum pump and the pump was run for about 3 to 4 hours. When the vacuum of the order of 10^{-3} to 10^{-4} mm Hg pressure was obtained, which was measured by a Macleod gauge, stopcock S10 was closed and S11 and S12 were opened. Now high purity nitrogen gas (Industrial Gases, Kanpur; Laboratory grade 99.5% & over purity) was bled until the pressure shown in the manometer, as viewed visually, was between 600 to 700 mm Hg pressure, so as to enable the feeding of the samples under vacuum.

The feeding device consisted of a round bottom flask of 100 cm^3 capacity provided with a stopper having two one-way stopcocks at right angles to each other. About 80-90 cm^3 of feed of known composition was taken into the flask and fed into the contactor (about 30-35 cm^3) and vaporizer units (about 50-55 cm^3) of the still under nitrogen atmosphere through stopcocks S1 and S2 respectively. In this fashion contamination of the sample by air was avoided.

The ebulliometric liquid, analar grade acetone supplied by British Drug House, India with a stated purity of 99.5 mole% or better was fed into the ebulliometer in the same way as above through stopcock S6.

3. Operation of the Equilibrium Still:

Immediately after feeding the samples, the pressure in

the system was increased roughly to 760 mm Hg by bleeding
nitrogen gas. Heater H_1 and H_2 were put on and the voltage
was appropriately increased in small increments. The voltage
to the heater H_2 of the ebulliometer was adjusted to obtain
proper condensation rate (between 10 to 20 drops/minute).

With increasing voltage to the still the liquid in the
vaporizer started vaporizing and kept bubbling through the
slots into the liquid hold up and the mass transfer between
phases started taking place. When this phenomenon was
nearing completion, i.e. when the equilibrium was fast
approaching, the equilibrium vapor containing much of the
more volatile component started emanating from the liquid
phase and started condensing. The heat input to the heater
H_1 of the still was adjusted such that the condensation rate
was between 10 to 20 drops/minute.

The condensed vapor passed through the vaporizer unit,
got vaporized, bubbled through the liquid and condensed
again. This recirculation was allowed to continue to attain
stable equilibrium, which took between 1½ and 3 hours
depending upon the system and the temperature involved.

4. Measurement of Equilibrium Pressure and Temperature:

In the initial stages of heating, the pressure in the
system kept rising owing to the increase in the vapor pressure
of the samples in the still and the ebulliometer with the
increase in temperature and stopped after condensation
started.

The pressure in the system and heat input to the ebulliometer were simultaneously adjusted such that the liquid in it boiled within $\pm$ 0.01°C of its normal boiling point, which is an indication of the fact that the system is at 760 $\pm$ 0.2 mm Hg pressure.

Precise measurement of equilibrium temperatures was carried out with the help of a chromel-alumel thermocouple. The voltage developed across its junctions was measured by a Honeywell potentiometer, which could read voltage upto three decimal places. (Corresponding to an accuracy of $\pm$ 0.02 °C in temperature). The thermocouple was calibrated against a platinum resistance thermometer, the details of which are given in Appendix A.

The hot junctions of the thermocouples TC1 and TC2 were immersed in the respective thermowells of the still and the ebulliometer containing silicone oil meant for rapid thermal contact. The cold junctions of the thermocouples were maintained within $\pm$ 0.01°C of the triple point of ice by immersing them in dewar flasks containing a slurry of ice and water. Sufficient care was taken to avoid air gaps.

5. Analysis of Equilibrium Liquid and Vapor Samples:

When equilibrium was attained, which is ensured by the constancy of the voltage in the potentiometer, the liquid and vapor samples were withdrawn through stopcocks S1 and S2 respectively into a five ml capacity sample tubes provided

with air tight caps. These were collected after flushing
out some liquid to avoid contamination. While collecting
vapor sample, stopcock S2 was opened in such a way that the
sample was withdrawn from the condenser.unit and not from
the vaporizer unit. In the case of dichloromethane-methanol
system, the sample tubes were kept in an ice flask imme-
diately after withdrawal to avoid vaporization losses.

The samples were analysed for their composition by
measuring the refractive indices with the help of a " Bausch
and Lomb" refractometer (mole fraction reproducible upto
± .001). Both the binary systems were calibrated earlier for
refractive index versus mole fraction, the details of which
are given in Appendix B.

The refractive index data were noted at a consultant
temperature of 25 ± 0.1°C by circulating water through the
refractometer prism, with the help of a constant temperature
bath.

EXPERIMENTAL RESULTS, THERMODYNAMIC
CONSISTENCY AND ERROR ANALYSIS

1. EXPERIMENTAL RESULTS:

The experimental and smoothened t-x-y data for the
dichloromethane-methanol system and the methanol-2-butanol
system are presented in tables I, II, III and IV respectively.
The t-x-y plots of both the systems are shown in Figs. 4 and
6. The y-x plots are shown in Figs. 5 and 7.

2. THERMODYNAMIC CONSISTENCY:

The vapor-liquid equilibrium data are subject to errors
depending upon the type of the instrument used and the accuracy
of measurement. Though the smoothness of the t-x-y plot
identifies the random errors, it does not guarantee the
reliability of the experimental data. Hence, there is a need
for checking the consistency of the data using a thermo-
dynamically exact relation - the Gibbs-Duhem equation.

The Gibbs-Duhem equation interrelates the activity
coefficients of all the components in a mixture and its most
general form for a binary system is given below:

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} + \frac{h^E}{RT^2} \frac{dT}{dx_1} + \frac{v^E}{RT} \frac{dP}{dx_1} = 0$$

$$(5.1)$$
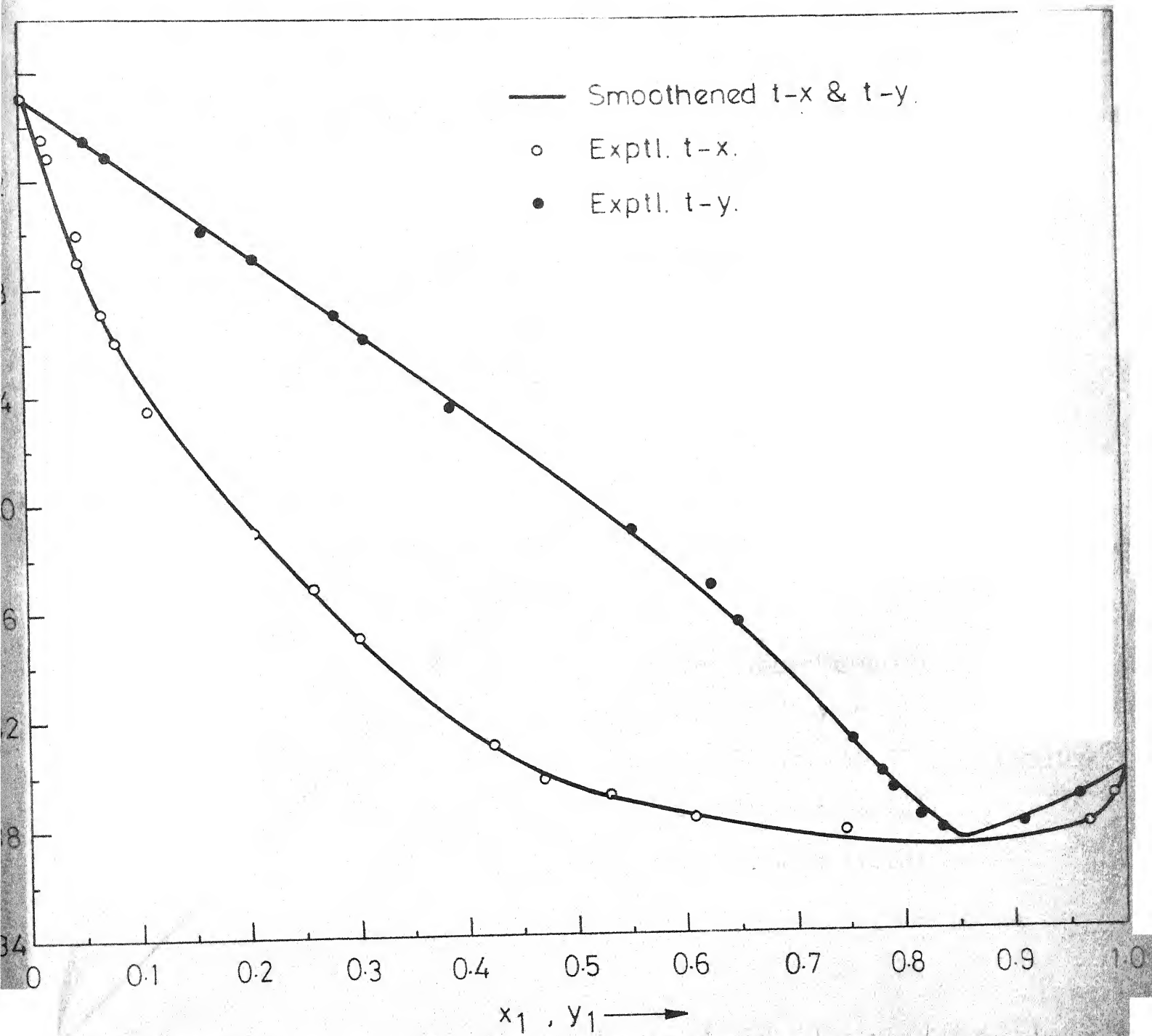
Fig. 4 – t-x-y diagram for Dichloromethane (1)-Methanol (2) system at 760 mm. mercury pressure.
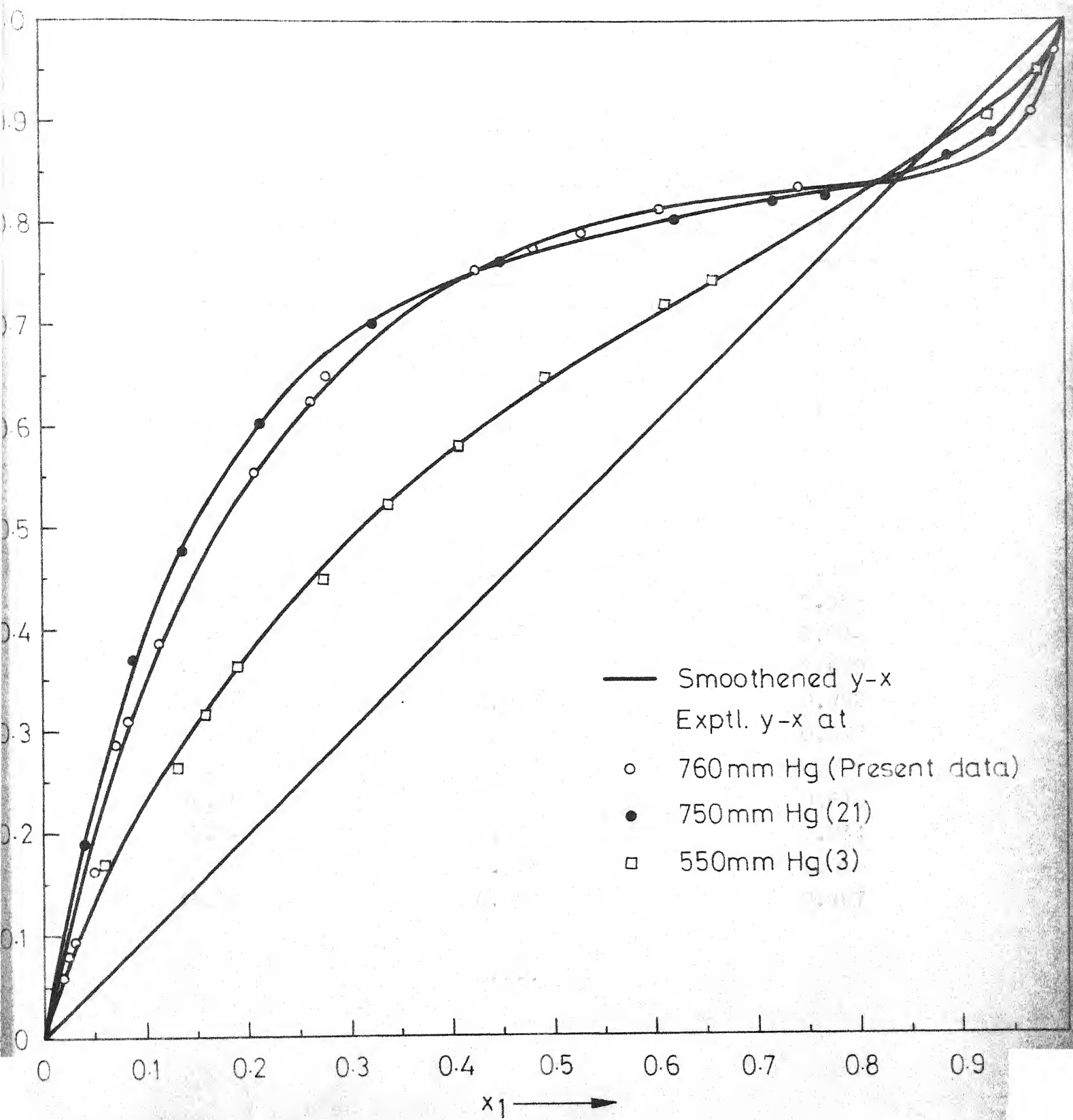
Fig. 5 – y-x diagram for Dichloromethane (1) + Methanol (2) system different pressures.

TABLE I

EXPERIMENTAL t-x-y DATA FOR DICHLOROMETHANE (1)-METHANOL (2) SYSTEM AT 760 mm MERCURY PRESSURE

t°C	x_1	y_1
63.46	0.022	0.058
62.98	0.025	0.080
62.65	0.032	0.087
60.04	0.052	0.163
59.15	0.050	0.215
57.04	0.071	0.285
56.11	0.084	0.309
53.54	0.113	0.387
48.95	0.211	0.555
46.92	0.263	0.624
45.56	0.277	0.650
41.05	0.427	0.752
39.86	0.470	0.777
39.22	0.530	0.789
38.18	0.606	0.815
37.64	0.744	0.834
37.89	0.968	0.910
38.94	0.991	0.967

. . . .

TABLE II

SMOOTHENED t-x-y DATA FOR DICHLOROMETHANE (1)-

METHANOL (2) SYSTEM AT 760 mm MERCURY PRESSURE

t°C	x_1	y_1
64.00	0.023	0.033
63.00	0.021	0.069
62.00	0.024	0.105
61.00	0.030	0.142
60.00	0.038	0.178
59.00	0.049	0.214
58.00	0.062	0.249
57.00	0.075	0.284
55.00	0.089	0.353
54.00	0.140	0.387
53.00	0.135	0.420
52.00	0.151	0.452
51.00	0.168	0.484
50.00	0.185	0.515
49.00	0.203	0.546
48.00	0.222	0.575
47.00	0.242	0.644
46.00	0.265	0.632
45.00	0.291	0.658
44.00	0.321	0.684
43.00	0.354	0.709
42.00	0.393	0.732
41.00	0.437	0.755
40.00	0.489	0.776
39.00	0.549	0.796
38.00	0.618	0.815
37.60	0.697	0.830
38.00	0.970	0.910
39.00	0.993	0.965
39.50	0.998	0.988

. . . .
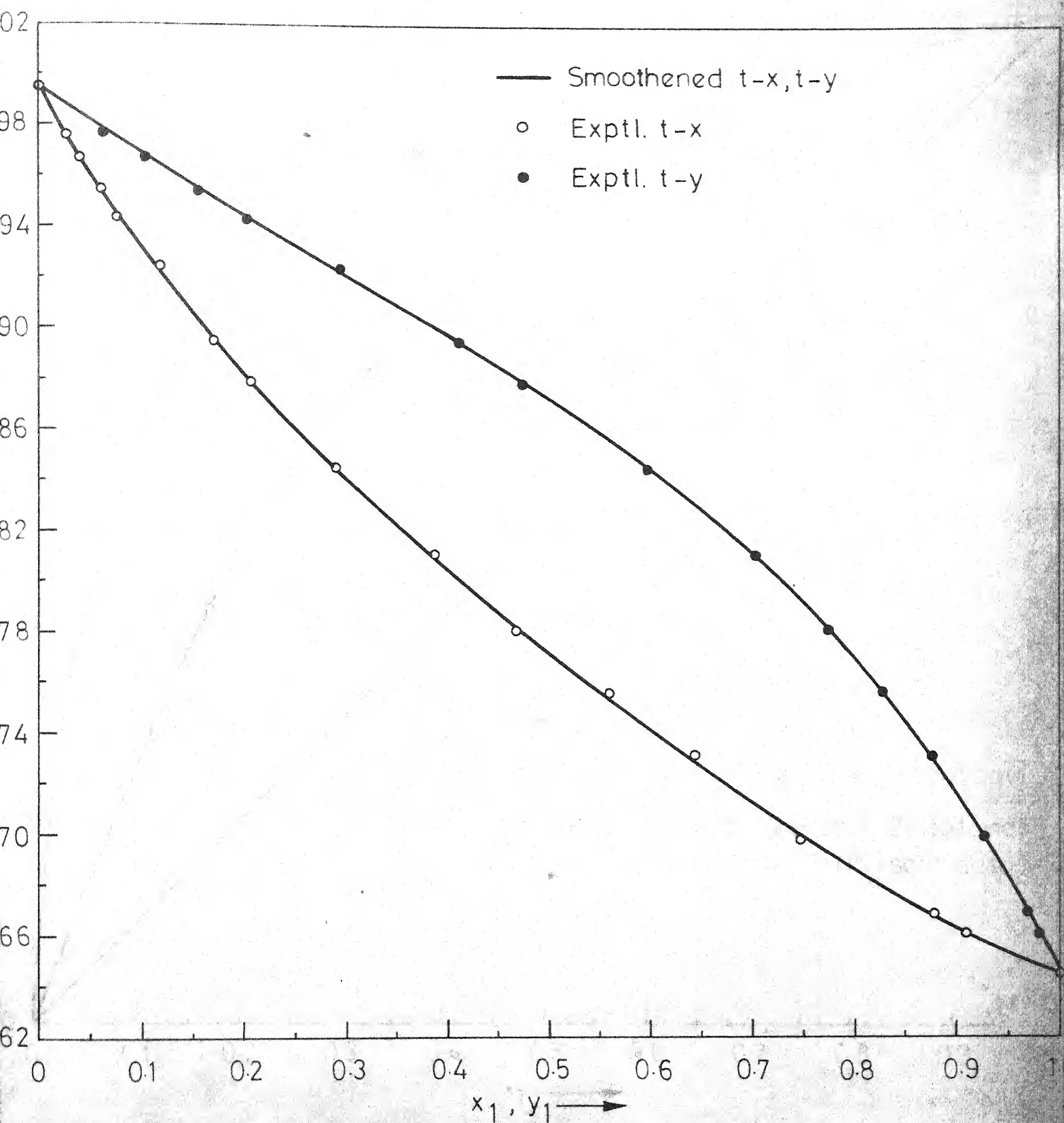
Fig. 6 – t–x–y diagram for Methanol (1)–2– Butanol (2) system at 760 mm. mercury pressure.
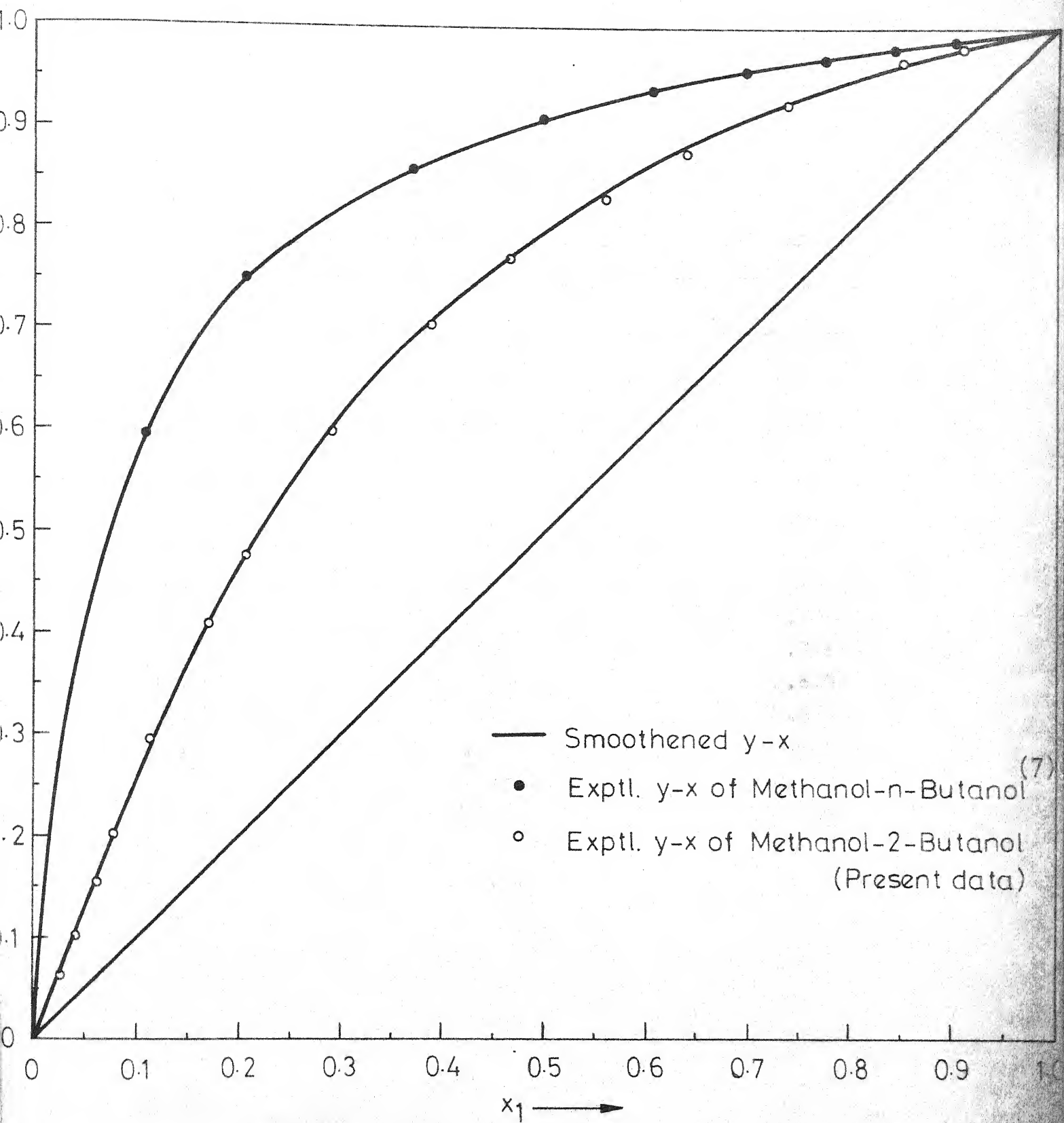
Fig. 7 - y-x diagram for Methanol (1) - Butanol (2) system at 760 mm mercury pressure.

TABLE III

EXPERIMENTAL t-x-y DATA FOR METHANOL (1) -2-
BUTANOL (2) SYSTEM AT 760 mm MERCURY PRESSURE

t°C	x_1	y_1
97.55	0.027	0.062
96.75	0.042	0.104
95.38	0.062	0.155
94.27	0.076	0.204
92.38	0.118	0.295
89.50	0.171	0.410
87.90	0.206	0.476
84.45	0.292	0.600
81.00	0.390	0.704
78.11	0.467	0.772
75.59	0.560	0.829
73.15	0.643	0.877
69.87	0.746	0.927
66.94	0.878	0.967
66.08	0.910	0.980

. . . .

TABLE IV

SMOOTHENED t-x-y DATA FOR METHANOL (1) -2-BUTANOL(2) SYSTEM AT 760 mm MERCURY PRESSURE

t°C	x_1	y_1
99.00	0.008	0.020
98.00	0.022	0.058
97.00	0.037	0.095
96.00	0.052	0.142
95.00	0.068	0.187
94.00	0.085	0.231
93.00	0.102	0.274
92.00	0.124	0.316
91.00	0.139	0.356
90.00	0.159	0.396
89.00	0.180	0.434
88.00	0.201	0.471
87.00	0.224	0.507
86.00	0.247	0.541
85.00	0.272	0.575
84.00	0.298	0.607
83.00	0.324	0.638
82.00	0.352	0.668
81.00	0.380	0.696
80.00	0.409	0.724
78.00	0.470	0.775
77.00	0.502	0.799
76.00	0.534	0.822
74.00	0.600	0.863
73.00	0.634	0.883
72.00	0.670	0.900

Table IV continued

t°C	x_1	y_1
71.00	0.706	0.917
70.00	0.743	0.933
69.00	0.783	0.947
68.00	0.825	0.960
67.00	0.870	0.972
66.00	0.919	0.982
65.00	0.973	0.992

. . . .

where h^E and v^E are the excess molar enthalpy and excess molar volume, respectively.

In general the experimental vapor-liquid equilibrium data for a binary system are taken either at isobaric or isothermal conditions. Therefore, for the two particular cases, Eqn.(5.1) reduces to the following forms:

(i) At constant temperature (Isothermal data):

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} + \frac{v^E}{RT} \frac{dP}{dx_1} = 0 \qquad (5.2)$$

(ii) At constant pressure (Isobaric data):

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} + \frac{h^E}{RT^2} \frac{dT}{dx_1} = 0 \qquad (5.3)$$

In the case of isothermal data, at low densities the effect of pressure on activity coefficients represented by the excess molar volume (third term in Eqn. (5.2)) is small and can in general, be neglected.

But in the case of isobaric data, which is pertinent to our study, the effect of temperature on activity coefficient given by the excess enthalpy of mixing term (third term in Eqn. (5.3)) cannot altogether be neglected. This is particularly true when the boiling point separation of the two components is large, molecules are not chemically similar, and if an azeotrope is formed. This is a serious limitation, since the excess enthalpy of mixing data are seldom available. It is a limitation which cannot otherwise be overcome.

Therefore, at best the consistency test can only be approximate after neglecting the enthalpy of mixing term. Eqn.(5.3) after re-arranging (neglecting the enthalpy of mixing term) reduces to the following form:

$$\int_{0}^{1} \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \qquad (5.4)$$

Hence for thermodynamic consistency the area under the curve of $\ln \frac{\gamma_1}{\gamma_2}$ vs x_1 should add to zero.

This integral area test failed for both the dichloro-methane-methanol and for methanol-2-butanol systems as will be shown later.

Herrington (16) has given a semi-empirical test for the isobaric case, in the absence of enthalpy of mixing data. Instead of assuming the excess enthalpy of mixing to be zero, he replaced it by the algebraic sum of the positive and negative areas under the curve $\ln \gamma_1 / \gamma_2$ vs x_1, represented by, I. Hence Eqn. (5.4) can be written as follows:

$$\int_{0}^{1} \ln \frac{\gamma_1}{\gamma_2} dx_1 = I \qquad (5.5)$$

If the sum of the magnitudes of positive and negative areas (without regard to sign) is denoted by Σ, then the percentage deviation D, is defined as:

$$D = \frac{100 \, |I|}{|\Sigma|} \qquad (5.6)$$

Fig. 8 – Plot of "ln γ_1/γ_2 vs. x (1)" for Dichloromethane (1) – Methanol (2) system at 760mm mercury pressure.
(Vertical lines indicate the error at each point)

$$J = \frac{150 \times 27.15}{310.55} = 13.1$$

$$D-J = 38.5 - 13.1 = 25.4$$

Hence $(D-J) > 10$. Therefore the data according to Herrington are probably not consistent.

b. Methanol-2-Butanol System:

The plot of ln γ_1 / γ_2 vs x_1 is shown in Fig. 9 and the data are presented in Table IX. The activity coefficients in this case were calculated assuming the vapor phase to be ideal ($\emptyset = 1.$) for the following reasons.

1. The experimental data for the second virial coefficients of 2-butanol were available from 378° to 423°K. The experimental temperatures involved are 337 to 373°K. In general extrapolations for prediction beyond the experimental range could give large errors in the B_V values. The experimental B_V data are shown in Table V. 2. The theoretical correlations of Pitzer and Curl (15) and that of Kreglewiski (10) when applied for predicting the second virial coefficients gave values which deviated considerably from the experimental values as shown in Table V. Hence it was assumed that $\emptyset_1 = \emptyset_2 = 1.$

From Fig. 9, the area above the x-axis, $I_1 = 0.064$. The area below the x-axis $I_2 = .028$. Since the total area under the curve does not add to zero, the criterion for consistency given by Eqn. (5.5) fails.
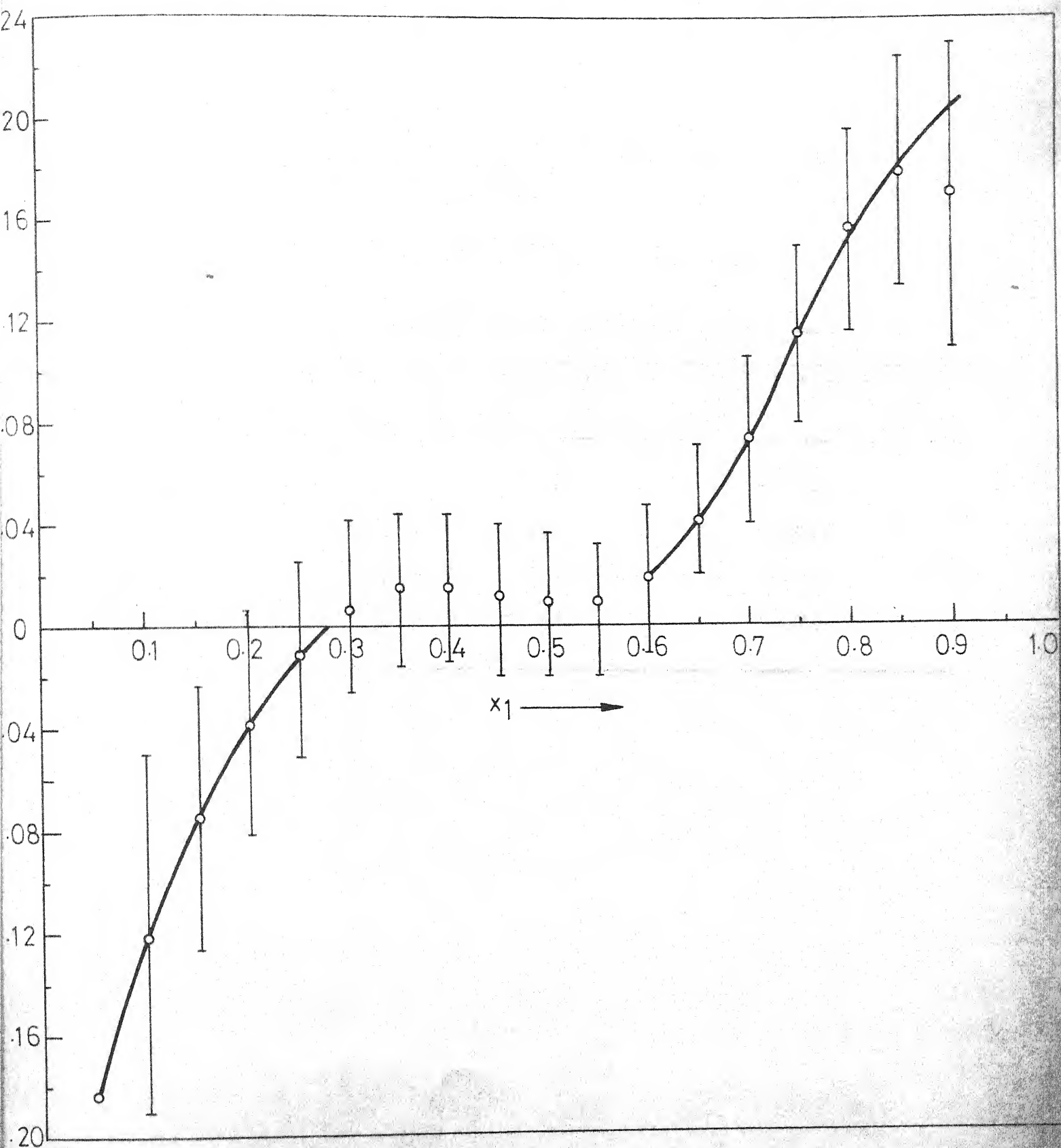
Fig. 9 - Plot of "ln ν_1/ν_2. vs. x (1)" for Methanol (1) - 2 - Butanol (1) system at 760 mm mercury pressure.

(Vertical lines indicate the error at each point)

TABLE V

SECOND VIRIAL COEFFICIENTS OF 2-BUTANOL

t °K	B(cc/gm mole)		
	Experimental data (4)	Predicted Data	
		Pitzer and Curl's (15) Model	Kreglewiski's (10) Model
378.2	−1131± 8	135.0	−754.0
393.2	− 969± 10	368.0	−688.0
408.2	− 831± 18	536.0	−630.0
423.2	− 692± 12	−50.4	−579.0

Applying the semi-empirical test of Herrington, we have,

$$I = I_1 - I_2 = 0.064 - 0.028 = 0.036 \text{ units of area}$$

$$\Sigma = I_1 + I_2 = 0.064 + 0.028 = 0.092 \text{ units of area}$$

$$\Theta = 99.40 - 64.55 = 34.85 \text{ deg}$$

$$T_{min} = 64.55 + 273.15 = 339.70°K$$

$$D = \frac{100 \times 0.036}{0.092} = 39.2$$

$$J = \frac{150 \times 34.85}{337.70} = 15.4$$

$$D-J = 39.2 - 15.4 = 23.8$$

Therefore, the data for this system also do not satisfy the Herrington's criteria for thermodynamic consistency.

The phsyical properties relevant for the calculation of the activity coefficients are given in Appendix IV. Also the values of the second virial coefficients, the fugacity coefficients and the liquid molar volumes at the required temperatures for the dichloromethane-methanol system are given in Appendix V.

3. ERROR ANALYSIS:

As had been mentioned earlier the vapor-liquid equilibrium data are susceptible to errors and hence it would be worthwhile to consider the effect of the errors in the measurement of temperature, pressure and composition of the liquid and vapor phases on the magnitudes of activity coefficients.

In general if we have a quantity F, given by

$$F = f(Z_1, Z_2 \text{--------} Z_n) \qquad (5.8)$$

then, according to the general formula of error propogation, F, the absolute error in F is given by

$$\delta F = \frac{\partial f}{\partial Z_1} \delta Z_1 + \frac{\partial f}{\partial Z_2} \delta Z_2 + \ldots + \frac{\partial f}{\partial Z_n} \delta Z_n \qquad (5.9)$$

and since the errors in the independent variable can be either positive or negative, it is necessary that one should take the absolute value of the errors contributed by each independent variable. Hence

$$\delta F = \left| \frac{\partial f}{\partial Z_1} \right| \delta Z_1 + \left| \frac{\partial f}{\partial Z_2} \right| \delta Z_2 + \ldots + \left| \frac{\partial f}{\partial Z_n} \right| \delta Z_n \qquad (5.10)$$

In the particular case of the activity coefficient γ_1 of a component one in a binary system is given by Eqn.(5.11) by assuming $\emptyset_i = 1$ and $f_i^{ol} = p_i^s$.

$$\gamma_i = \frac{y_i\, P}{x_i\, P_i{}^s} \qquad (5.11)$$

The error in $\ln \gamma_1$, applying the general formula given by Eqn.(5.10), is given by Eqn. (5.12).

$$\delta(\ln \gamma_1) = \left| \frac{\delta \gamma_1}{\gamma_1} \right| = \left| \frac{\delta y_1}{y_1} \right| + \left| \frac{\delta P}{P} \right| + \left| \frac{\delta x_1}{x_1} \right| + \left| \frac{\delta P_1^s}{P_1^s} \right| \qquad (5.12)$$

and since $\ln(\gamma_1/\gamma_2) = \ln \gamma_1 - \ln \gamma_2$

$$\delta(\ln(\gamma_1/\gamma_2)) = \left| \delta(\ln \gamma_1) \right| + \left| \delta(\ln \gamma_2) \right| \qquad (5.13)$$

In the present study, the error in x was chosen
as the independent error and the error in y and T as the
dependent errors. That is

$$y = f(x) ; \quad T = f(x) \tag{5.14}$$

Therefore, the errors in y and T are

$$\delta y = \frac{dy}{dx} \delta x; \quad \delta T = \frac{dT}{dx} \delta x \tag{5.15}$$

where the slopes dy/dx and dT/dx were obtained by differen-
tiating the polynomial functions of y and T in terms of x.
These values are presented in Tables VI and VII.

δP in Eqn. (5.12) is the error in the measurement
of total pressure which depends upon the error in the
measurement of the ebulliometric temperature. δP_i^S , the
error in the pure component vapor pressure is,

$$\delta P_1^S = \frac{dP_1^S}{dT} \delta T \tag{5.16}$$

The derivative $\frac{dP_1^S}{dT}$ was obtained by differentiating
the Antoine equation for that particular component.

Since all the quantities on the right hand side of
Eqn. (5.12) are known, the error in ln γ_1 and similarly
the error in ln γ_2 and hence also the error in ln(γ_1/γ_2)
were calculated.

The errors involved in the individual values of ln γ_1,
ln γ_2 and ln (γ_1/γ_2) for both the binary system are
given in Tables VIII and IX. The magnitudes of errors are
also plotted as vertical lines in Figs. 8 and 9.

TABLE VI

DERIVATIVES OF VAPOR COMPOSITION AND EQUILIBRIUM TEMPERATURES WITH RESPECT TO LIQUID COMPOSITION FOR DICHLOROMETHANE (1) - METHANOL (2) SYSTEM AT 760 mm MERCURY PRESSURE

x_1	dy/dx	dT/dx
0.010	5.908	-147.965
0.024	5.093	-132.551
0.033	4.637	-123.583
0.040	4.339	-18.796
0.050	3.867	-107.752
0.060	3.500	- 99.813
0.070	3.190	- 92.615
0.100	2.450	- 74.981
0.150	1.772	- 56.096
0.200	1.447	-46 .084
0.250	1.238	- 40.909
0.300	1.030	- 37.519
0.350	0.794	- 33.842
0.400	0.530	- 28.787
0.450	0.380	- 22.244
0.500	0.299	- 15.087
0.550	0.324	- 9.166
0.600	0.390	- 7.318
0.650	0.330	- 13.356
0.700	0.158	- 32.080
0.840	-	-
0.970	0.763	. 1.01
0.980	2.257	39.394
0.990	3.753	79.798

TABLE VII

VALUES OF $\frac{dy}{dx}$ and $\frac{dT}{dx}$ FOR METHANOL (1) -2-

BUTANOL (2) SYSTEM AT 760 mm MERCURY PRESSURE

x_1	$\frac{dy}{dx}$	$\frac{dT}{dx}$
0.05	2.637	-64.371
0.10	2.391	-56.584
0.15	2.094	-50.308
0.20	1.786	-45.300
0.25	1.497	-41.367
0.30	1.245	-38.310
0.35	1.038	-35.950
0.40	0.877	-34.123
0.45	0.759	-32.682
0.50	0.675	-31.492
0.55	0.614	-30.438
0.60	0.564	-29.417
0.65	0.517	-28.343
0.70	0.463	-27.148
0.75	0.400	-25.769
0.80	0.330	-24.173
0.85	0.266	-22.330
0.90	-0.258	-20.240
0.95	0.246	-17.901

. . . .

TABLE VIII

VALUES OF ACTIVITY COEFFICIENTS ALONG WITH THE ERRORS INVOLVED IN INDIVIDUAL VALUES OF γ FOR DICHLOROMETHANE (1)-METHANOL (2) SYSTEM AT 760 mm MERCURY PRESSURE

x_1	$\ln \gamma_1$	$\delta(\ln \gamma_1)$	$\ln \gamma_2$	$\delta(\ln \gamma_2)$	$\ln \dfrac{\gamma_1}{\gamma_2}$	$\delta(\ln \dfrac{\gamma_1}{\gamma_2})$
0.010	0.199	0.655	0.013	0.064	0.187	0.719
0.024	0.387	0.552	0.021	0.059	0.367	0.561
0.033	0.528	0.363	0.030	0.057	0.496	0.360
0.038	0.710	0.304	0.035	0.055	0.675	0.359
0.050	0.769	0.216	0.055	0.052	0.714	0.138
0.060	0.865	0.175	0.059	0.049	0.826	0.224
0.070	0.870	0.146	0.067	0.047	0.803	0.193
0.100	0.780	0.096	0.101	0.041	0.679	0.138
0.150	0.728	0.063	0.139	0.035	0.589	0.097
0.200	0.679	0.047	0.169	0.032	0.510	0.079
0.250	0.642	0.038	0.191	0.032	0.451	0.070
0.300	0.613	0.032	0.211	0.031	0.240	0.062
0.350	0.586	0.026	0.240	0.229	0.345	0.055
0.400	0.553	0.022	0.280	0.026	0.267	0.048
0.450	0.511	0.018	0.353	0.023	0.159	0.041
0.500	0.461	0.015	0.429	0.021	0.031	0.036
0.550	0.406	0.013	0.500	0.022	-0.094	0.035
0.600	0.354	0.013	0.554	0.025	-0.200	0.038
0.650	0.314	0.013	0.613	0.028	-0.300	0.040
0.700	0.288	0.015	0.786	0.030	-0.498	0.044

Table VIII continued

x_1	$\ln \gamma_1$	$\delta(\ln \gamma_1)$	$\ln \gamma_2$	$\delta(\ln \gamma_2)$	$\ln \frac{\gamma_1}{\gamma_2}$	$\delta(\ln \frac{\gamma_1}{\gamma_2})$
0.840	0.108	–	1.383	–	-1.274	–
0.970	0.003	0.010	2.451	0.210	-2.445	0.220
0.980	0.002	0.025	2.668	0.411	-2.666	0.436
0.990	0.001	0.400	2.826	0.938	-2.826	0.977

. . . .

TABLE IX

VALUES OF ACTIVITY COEFFICIENTS ALONG WITH THE ERRORS INVOLVED IN INDIVIDUAL VALUES OF γ FOR METHANOL (1) – 2-BUTANOL (2) SYSTEM AT 760 mm MERCURY PRESSURE

x_1	$\ln \gamma_1$	$\delta(\ln \gamma_1)$	$\ln \gamma_2$	$\delta(\ln \gamma_2)$	$\ln \frac{\gamma_1}{\gamma_2}$	$\delta(\ln(\gamma_1/\gamma_2))$
0.050	−0.147	0.211	0.036	0.033	−0.183	0.244
0.100	−0.072	0.106	0.049	0.033	−0.121	0.140
0.150	−0.028	0.071	0.046	0.033	−0.040	0.104
0.200	−0.003	0.052	0.035	0.033	−0.075	0.055
0.250	0.009	0.041	0.020	0.032	−0.011	0.073
0.300	0.012	0.034	0.006	0.032	0.006	0.066
0.350	0.011	0.023	−0.004	0.032	0.014	0.061
0.400	0.007	0.025	−0.008	0.033	0.015	0.051
0.450	0.004	0.023	−0.008	0.033	0.012	0.055
0.500	0.002	0.021	−0.007	0.034	0.009	0.055
0.550	0.002	0.019	−0.017	0.037	0.010	0.056
0.600	0.005	0.018	−0.014	0.034	0.019	0.067
0.650	0.010	0.016	−0.031	0.044	0.040	0.061
0.700	0.016	0.015	−0.059	0.050	0.073	0.065
0.750	0.019	0.014	−0.096	0.056	0.115	0.071
0.800	0.022	0.013	−0.135	0.065	0.156	0.078
0.850	0.021	0.012	−0.158	0.079	0.180	0.091
0.900	0.018	0.011	−0.152	0.108	0.170	0.120
0.995	0.013	0.011	−0.185	0.230	0.200	0.239

The activity coefficient composition data for both the binary systems were fitted to the following standard models:

1. Margule's two suffix Eqn.

2. Vanlaar's two constant Eqn.

3. Redlich-Kister's three constant Eqn.

4. Wilson's two parameter Eqn.

5. Three parameter Alpha Eqn.

None of the models ~~did fit~~ _fitted_ the data as the deviations were quite large.

DISCUSSION OF RESULTS AND CONCLUSIONS

Dichloromethane-Methanol System:

The following values for the azeotropic compositions
and their corresponding minimum boiling temperatures at different
pressures were available in the literature. Also included are
the data obtained in the present investigation.

1. At 760 mm Hg pressure:

   (a) $x_1 = 0.805$; $t = 38.8°C$ (19)

   (b) $x_1 = 0.840$; $t = 37.4°C$ (present data)

2. At 750 mm Hg pressure:

   $x_1 = 0.846$; $t = 37.2°C$ (21)

3. At 550 mm Hg pressure:

   $x_1 = 0.885$; $t = 28.9°C$ (3)

According to Sarma's data, $\left|\frac{dx_1}{dP}\right| = .0041$ and $\left|\frac{dT}{dP}\right| = .16$
for a fall in pressure 10 mm Hg. But with the present data
$\left|\frac{dx_1}{dP}\right| = .0006$ and $\left|\frac{dT}{dP}\right| = .02$ for the same change in pressure.
The magnitudes of $(\frac{dx_1}{dP} , \frac{dT}{dP})$ of the latter data seem to be
of comparable value with the data for a fall in pressure from
750 to 550 mm Hg. where $\left|\frac{dx_1}{dP}\right| = .0002$ and $\left|\frac{dT}{dP}\right| = .0415$.

Hence the present data at 760 mm Hg pressure fall more

in line with the data of Tenn and Missen, and Chhotray, than what Sarma's data did. It was therefore felt that Sarma's data was affected by the presence of water in the methanol sample used in his work.

As mentioned in Chapter II the activity coefficients were calculated taking into consideration the vapor phase non-ideality. It was observed (see Appendix V) that the fugacity coefficients varied from 0.966 to 1.118 which shows the marked influence it has on the final magnitudes of the activity coefficients.

For facilitating a comparative study, the following plots were prepared (1) The activity coefficient vs. composition of the system at different pressures (See Fig.10) (2) The activity coefficient vs. composition of the chloromethanes-methanol systems (See Fig.11). The activity coefficients of the system at 750 mm Hg were not available in the data reported by Tenn and Missen (21) and hence they were calculated from the reported t-x-y data taking non-ideality in the vapor phase into consideration (See Table X). For confining ourselves to a uniformity in procedure, the same procedure was adopted in calculating the activity coefficients for 1. chloroform-methanol system, and 2. carbon tetrachloride-methanol system (see Tables XI and XII). The necessary pure component data used in arriving at these values of the activity coefficients along with the computed intermediate values like the virial
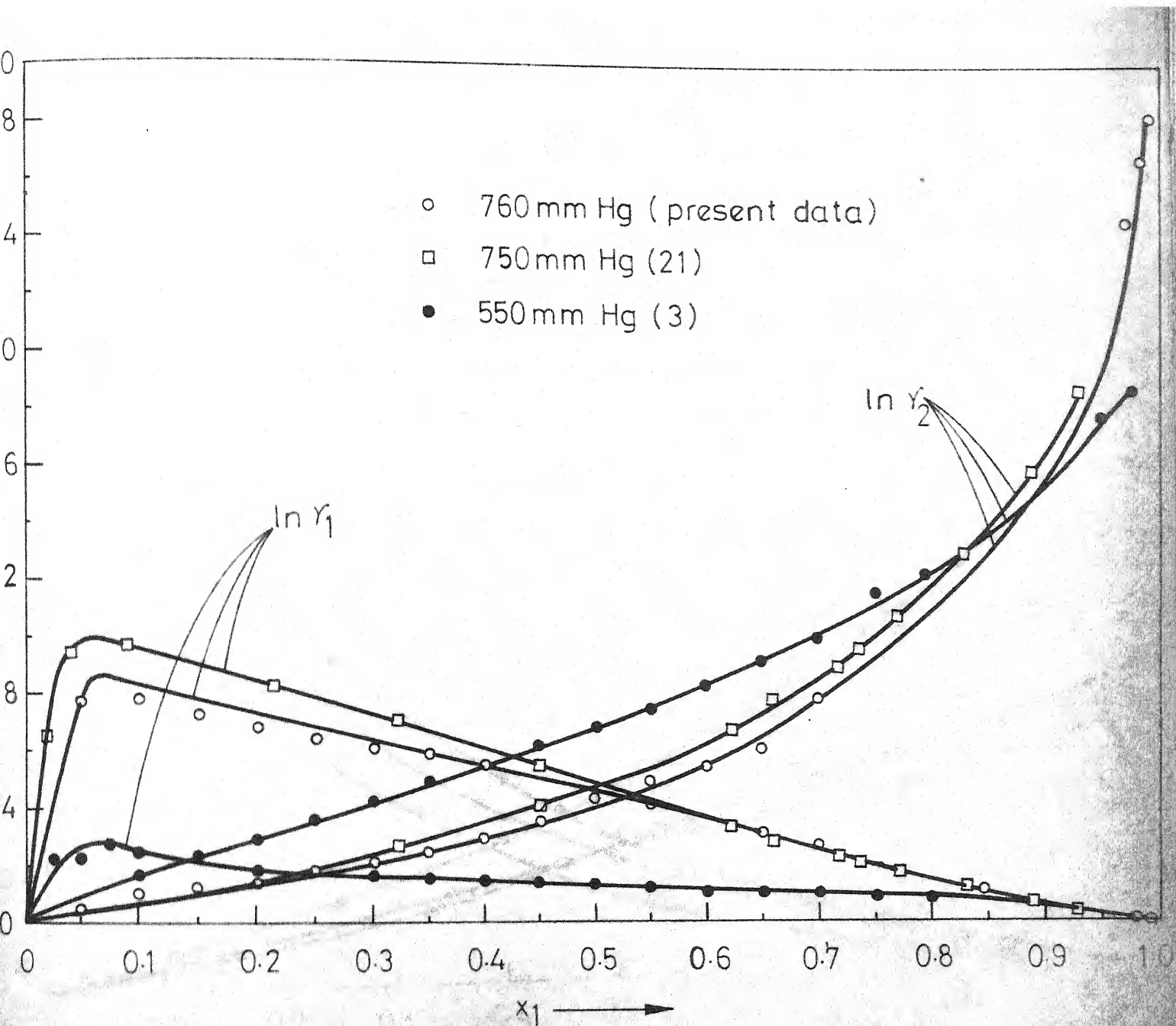
Fig. 10-Activity coefficient-composition diagram for Dichloromethane (1) Methanol (2) system at different pressures.
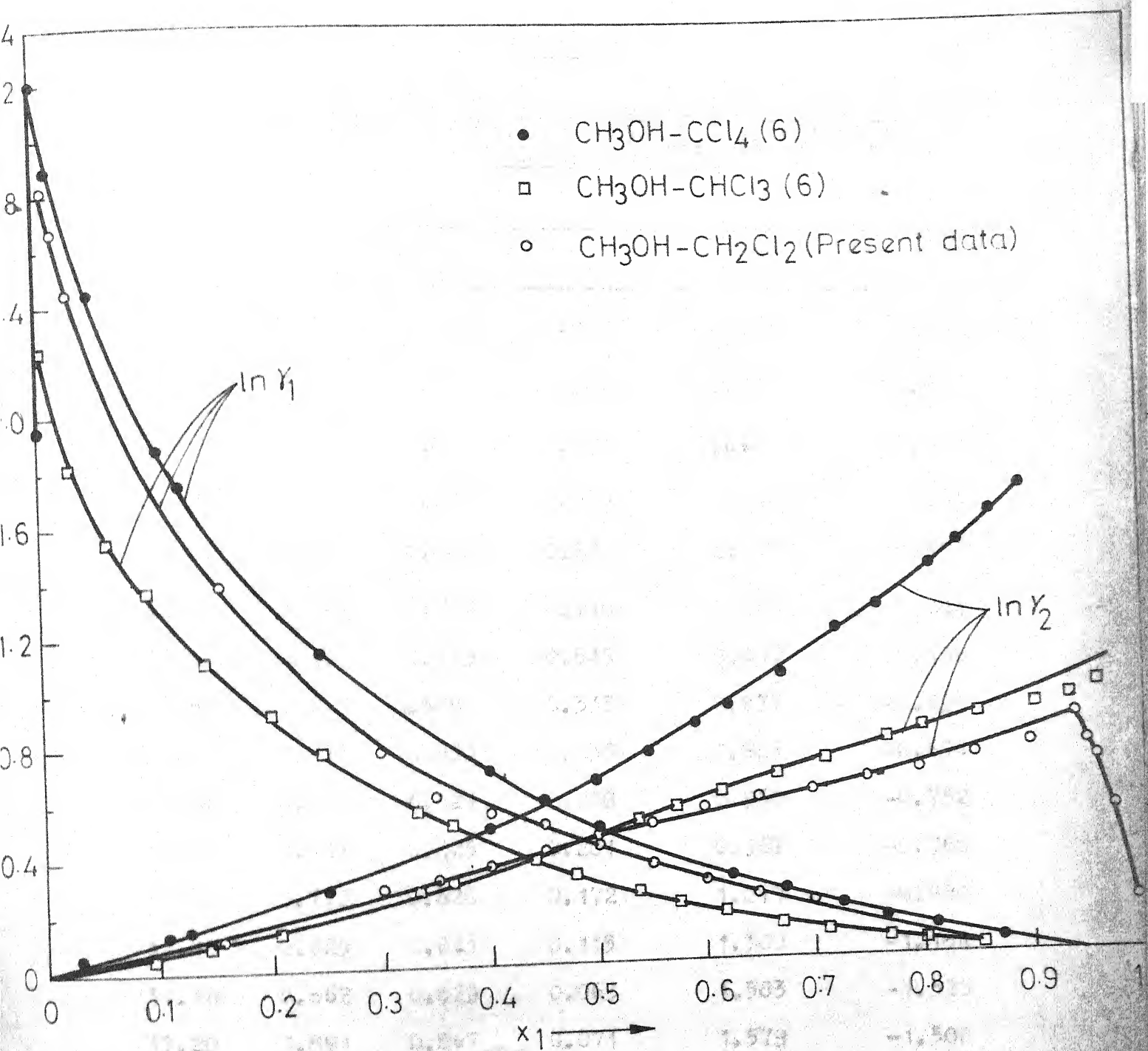
Fig.11 – Activity coefficient – composition diagram for Methanol(1)–Chloro methane (2) systems at 760 mm mercury pressure.

TABLE X

ACTIVITY COEFFICIENT COMPOSITION DATA FOR DICHLO-CHLOROMETHANE (1) - METHANOL (2) SYSTEM AT 750 mm MERCURY PRESSURE (21)

t°C	x_1	y_1	ln γ_1	ln γ_2	lnγ_1/γ_2
62.70	0.017	0.063	0.648	0.058	0.586
59.88	0.040	0.191	0.949	0.031	0.918
54.90	0.087	0.370	0.971	0.057	0.914
50.92	0.136	0.477	0.899	0.116	0.783
46.20	0.214	0.602	0.828	0.177	0.651
42.00	0.323	0.702	0.710	0.263	0.441
39.40	0.451	0.759	0.545	0.407	0.138
37.82	0.623	0.809	0.333	0.677	−0.498
37.38	0.717	0.623	0.233	0.886	−0.654
37.36	0.734	0.821	0.208	0.960	−0.752
37.36	0.742	0.825	0.201	0.969	−0.768
37.26	0.770	0.828	0.172	1.073	−0.920
37.18	0.829	0.841	0.115	1.300	−1.184
37.18	0.862	0.829	0.063	1.583	−1.520
37.20	0.891	0.867	0.071	1.579	−1.508
37.48	0.932	0.889	0.040	1.863	−1.823

TABLE XI

ACTIVITY COEFFICIENT COMPOSITION DATA FOR
METHANOL (1) - CHLOROFORM (2) SYSTEM AT
760 mm MERCURY PRESSURE (6)

t°C	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$	$\ln(\gamma_1/\gamma_2)$
60.50	0.005	0.035	2.246	-0.006	2.252
60.00	0.008	0.050	2.215	-0.002	2.217
59.50	0.010	0.068	2.245	-0.001	2.246
59.00	0.014	0.085	2.151	0.002	2.155
57.90	0.030	0.125	1.819	0.013	1.806
56.30	0.063	0.188	1.541	0.031	1.510
55.20	0.096	0.233	1.369	0.053	1.317
54.40	0.145	0.270	1.136	0.089	1.047
53.9	0.203	0.299	0.918	0.139	0.780
53.70	0.247	0.316	0.763	0.180	0.603
53.50	0.330	0.345	0.575	0.268	0.306
53.50	0.364	0.354	0.51.	0.303	0.207
53.50	0.372	0.357	0.496	0.311	0.184
53.70	0.443	0.381	0.372	0.389	-0.017
53.80	0.480	0.3 9.	0.316	0.436	-0.120
54.00	0.541	0.422	0.249	0.511	-0.262
54.30	0.575	0.436	0.209	0.552	-0.342
54.70	0.617	0.460	0.170	0.601	-0.431
55.30	0.668	0.493	0.128	0.664	-0.536
55.90	0.713	0.528	0.100	0.722	-0.622
57.00	0.770	0.580	0.063	0.796	-0.733
57.80	0.804	0.620	0.050	0.630	-0.779
59.30	0.854	0.696	0.031	0.866	-0.835
60.90	0.905	0.786	0.021	0.907	-0.886
62.00	0.935	0.846	0.013	0.932	-0.919
63.00	0.960	0.898	0.003	0.983	-0.979

TABLE XII

ACTIVITY COEFFICIENT COMPOSITION DATA FOR METHANOL (1) -CARBON TETRA CHLORIDE (2) SYSTEM AT 760 mm. MERCURY PRESSURE (6)

$t °C$	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$	$\ln(\gamma_1/\gamma_2)$
76.10	0.002	0.020	1.980	0.003	1.976
75.85	0.002	0.027	2.288	0.004	2.284
72.35	0.004	0.120	3.201	0.019	3.182
67.60	0.013	0.242	2.885	0.042	2.843
66.85	0.017	0.264	2.732	0.043	2.689
62.00	0.030	0.383	2.714	0.058	2.656
59.40	0.051	0.445	2.445	0.073	2.370
57.20	0.107	0.490	1.876	0.136	1.739
56.95	0.124	0.500	1.758	0.147	1.611
56.25	0.248	0.522	1.135	1.284	0.851
55.80	0.401	0.537	0.700	0.500	0.199
55.75	0.453	0.541	0.589	0.583	0.006
55.75	0.498	0.545	0.500	0.662	-0.162
55.70	0.505	0.549	0.494	0.671	-0.177
55.65	0.550	0.552	0.416	0.761	-0.344
55.70	0.597	0.558	0.343	0.856	-0.408
55.70	0.603	0.561	0.337	0.866	-0.513
55.70	0.603	0.561	0.337	0.866	-0.529
55.75	0.625	0.563	0.302	0.917	-0.614
55.75	0.676	0.576	0.245	1.035	-0.790
56.00	0.725	0.591	0.187	1.187	-0.969
56.00	0.727	0.595	0.191	1.155	-0.964
56.35	0.764	0.603	0.138	1.269	-1.131
56.75	0.813	0.630	0.099	1.422	-1.323
57.10	0.838	0.649	0.081	1.504	-1.423
57.70	0.868	0.677	0.059	1.609	-1.550
58.20	0.883	0.696	0.045	1.656	-1.611
58.60	0.897	0.760	0.040	1.704	-1.664

Table XII continued

t°C	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1 / \gamma_2)$
59.50	0.917	0.753	0.026	1.761	-1.735
60.40	0.938	0.803	0.027	1.800	- 1.7733
60.85	0.948	0.823	0.021	1.857	-1.836
61.80	0.962	0.864	0.013	1.883	-1.870
62.80	0.979	0.910	0.005	2.040	-2.035
63.50	0.986	0.939	0.000	2.039	-2.040
64.10	0.993	0.967	0.000	2.120	-2.123
64.50	0.997	0.988	0.000	1.932	-1.934
64.60	0.999	0.995	0.000	2.154	-2.155

coefficients, fugacity coefficients, etc. are given in Appendix IV and V.

From Fig. 10 it can be seen that at all the three pressures the activity coefficient of dichloromethane exhibits a maxima at about a composition of $x_1 = 0.05$ to 0.075, while that of methanol does not exhibit any minima. This phenomenon was also observed in carbon tetrachloride-methanol system at 760 mm Hg (See Fig. 11). In this system the activity coefficient of methanol exhibited a maxima at $x_1 < 0.01$. In the absence of h^E data it is difficult to analyze or comment on these data. However, this kind of behaviour may be attributed to the high degree of non-ideality of the particular systems due to the dipole-dipole interaction and hydrogen bonding of the constituent molecules.

It can also be noticed from Fig. 10 that as the pressure is decreased, the activity coefficient of methanol is higher upto $x_1 = 0.8$ and then crosses over the higher pressure data. This is not expected. Also the activity coefficient of dichloromethane does not follow a systematic pattern. This is also the case in the activity coefficients of chloromethanes-methanol systems (See Fig. 11). It was expected that the activity coefficient would follow a systematic trend as the chlorine constituent in the methane molecule is progressively increased or as the dipole moment decreases. However, no positive explanation can be given from the present and past results.

The general criteria for the consistency of the data - that the area above the x-axis should be equal to the area below the x-axis or Herrington's semi-empirical test seem to be failing in this case. Herrington's test is not rigorous and one cannot conclude that the data are inconsistent if they do not satisfy Herrington's test.

Methanol-2-Butanol System:

Fig. 12 shows that this system in general exhibits negative deviations from ideality unlike the methanol-n-butanol system (7) which shows positive deviations from ideality.

One also notices that the activity coefficients for both the components show slight positive deviations from ideality ($\ln \nu_1$ by .022 and $\ln \nu_2$ by 0.049 maximum). This deviation was more (see Fig. 12) in the case of methanol-n-butanol system where it exhibited negative deviations ($\ln \nu_2$ by 0.17 maximum.). This behaviour is in contradiction with the Gibbs-Duhem equation at constant T and P for according to it a system cannot both exhibit positive and negative deviation from ideality. Since the magnitudes of the activity coefficients are in general very sensitive to the variables like temperature, pressure and composition, any small amount of error in their measurement could amount to the above irregularity. Moreover the vapor-
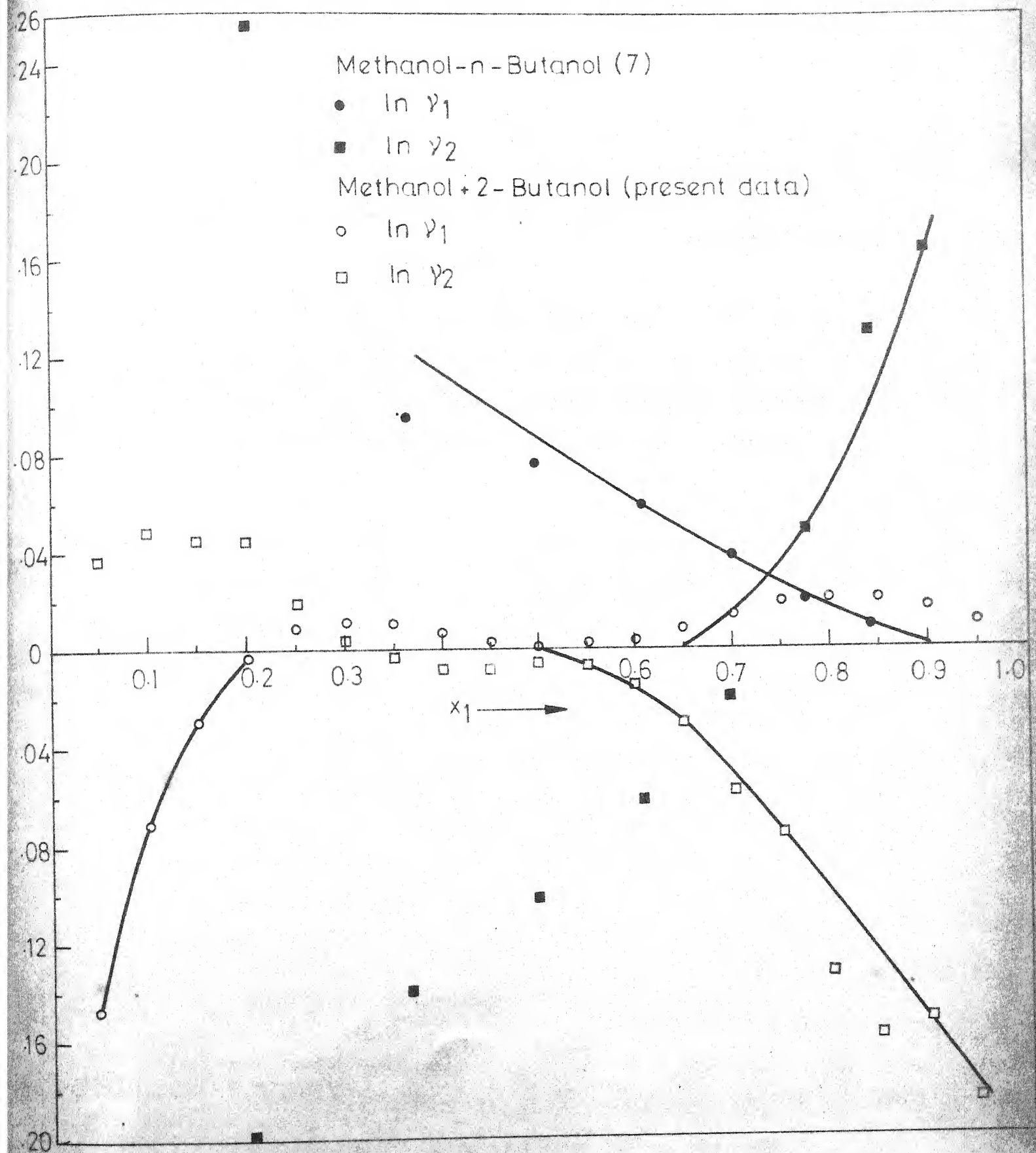
Fig.12 – Activity coefficient composition diagram for Methanol (1) – Butanol systems at 760 mm Hg pressure.

phase non-ideality should be taken into consideration in arriving at a proper assessment.

In this system also, since the enthalpy of mixing data were not available, nothing could be said about the consistency of the data. Because of actual magnitudes of γ s (see Table IX), this system may be considered ideal.

CHAPTER VII

EXCESS LIQUID MOLAR VOLUMES

The excess volumes of mixing are a measure of expansion or contraction when a mixture is formed from two liquids. The mixtures under investigation are expected to be non-ideal due to the polar nature of the molecules and hydrogen bonding in alcohols. Because of the nature of compounds involved in the present investigation, excess volumes of mixing were studied for dichloromethane-methanol and methanol-2-butanol systems at 25°C using pycnometry technique.

Description of the Apparatus:

The apparatus consisted of a modified Robertson (23) pycnometer immersed in a constant temperature bath. The bath had commercial ethylene glycol as bath fluid and the temperature of the bath was controlled to ± 0.01°C using a sargent thermo-meter. Each temperature was checked during the investigation with a chromel-alumel thermocouple and Honeywell potentiometer. A mettler balance capable of measuring weights upto ± .00001 gm was used for all weighings. The calibrating standard used was triple distilled mercury.   /

Experimental Procedure:

The binary mixture of known composition was filled upto the engraved marks on the two limbs of pycnometer and kept in the constant temperature bath. The bath temperature was

maintained at $25 \pm 0.02°C$. Intermittantly, the sample of same composition was either added or removed with the help of a syringe to keep the level in the pycnometer constant. The pycnometer was kept in the bath for about half an hour to attain equilibrium conditions. The pycnometer was taken out and the mixture was weighed after drying the outer surface properly. This procedure was repeated for all the readings.

Results:

The excess molar volume v^E i.e. the volume excess over the ideal volume of mixing is calculated according to the relationship:

$$v^E = \sum x_i M_i / d_{mix} - \sum \frac{x_i M_i}{d_i} \qquad (7.1)$$

or in terms of molar volumes $v^E = V_{mix} - \sum x_i v_i^0 \qquad (7.2)$

where

v^E = Excess molar volume,

V_{mix} = Actual molar volume,

v_i^0 = Molar volume of component i,

d_{mix} = density of the mixture,

d_i = density of component i, and

M_i = Molecular weight of component i.

The second term on the right hand side of Eqn.(7.1) or (7.2) gives the volumes of mixing if the mixtures were to behave ideally.

The air buoyancy corrections in the density range

studied amounted to 2 to 4 units in the fifth decimal place
and hence were not taken into consideration. The accuracy of
density measurements is estimated to be $\pm$ 0.0005 gms/cm^3.

The plot of excess molar volumes vs composition
is shown in Fig. 13 for both the systems and the data are
presented in Table XIII.

Discussion of the Results:

It can be noticed from Fig. 13 that in both the
systems, the actual volume of mixing is always greater than the
ideal volume of mixing. This can probably be due to the
following reasons. The hydrogen bonded alcohol molecules
associate between themselves to form clusters of molecules and
the other non-associating molecules do not provide the necessary
energy to break the clusters, with the result that there is
a net expansion in the volume. Also since in both the systems
the molecules are polar, the repulsive force between the
molecules seems to be predominant which could also be contri-
buting to the positive deviations from ideality.

No conclusive explanation can be given on the molecular
level for this behavior from the experimental data obtained in
this investigation.

. . . .
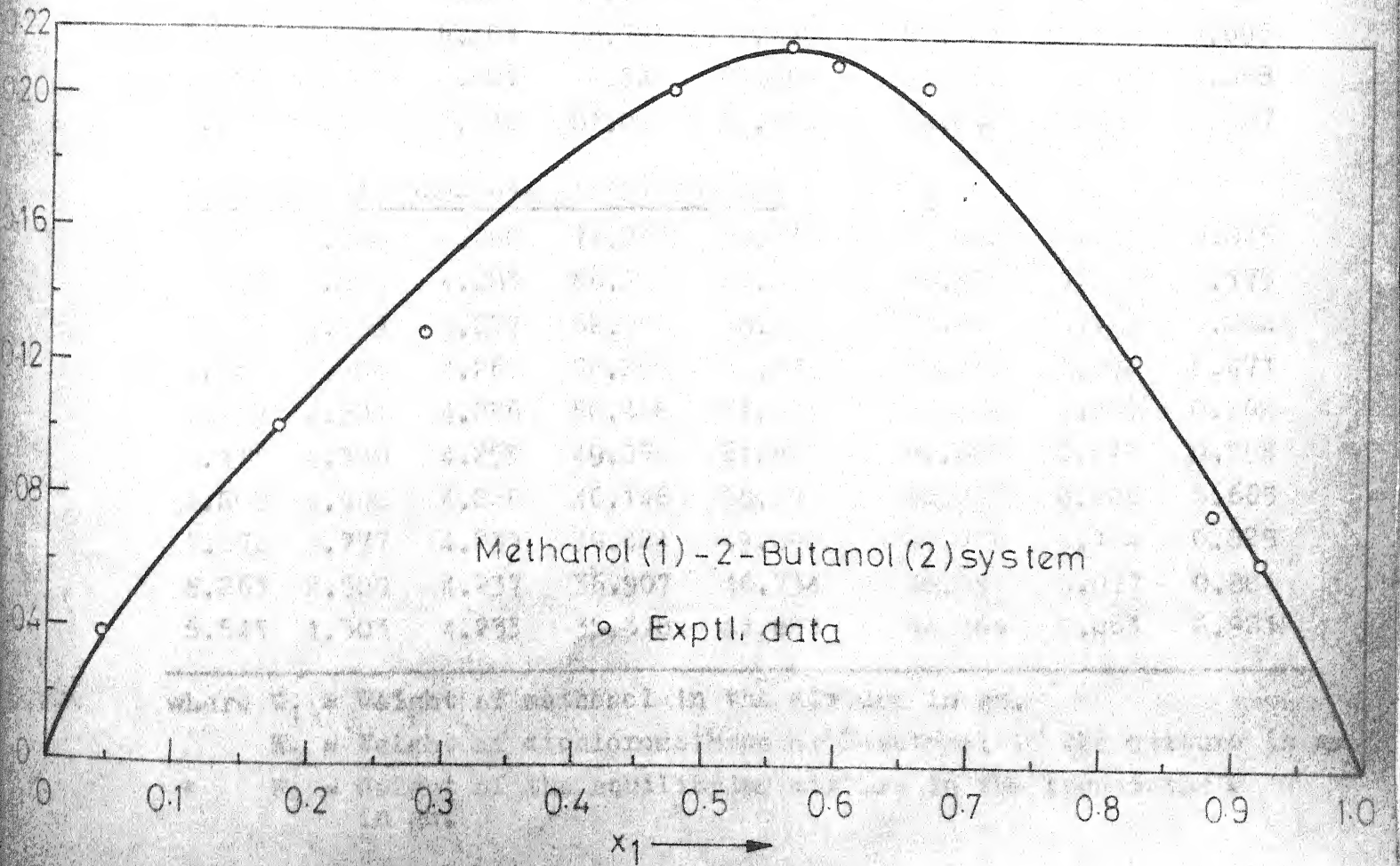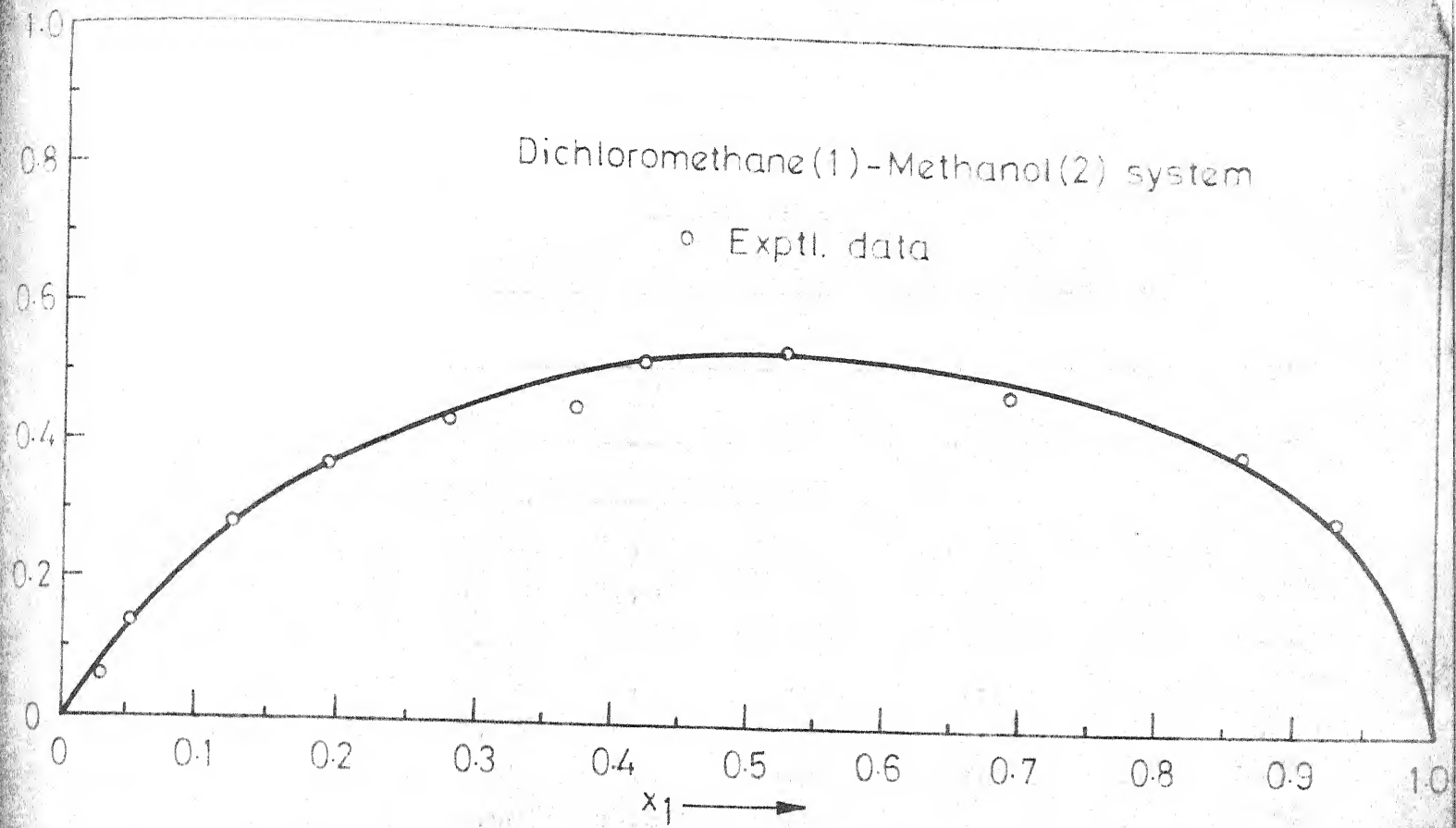
Fig.13-Excess molar volume vs composition diagrams.

TABLE XIII

EXCESS LIQUID MOLAR VOLUME DATA (25+.02°C)

W_1	W_2	W_3	AVM	V_{actual}	V_{ideal}	V^E	x_1
a. Dichloromethane(1)-Methanol(2) System							
20.357	1.580	4.349	33.536	41.372	41.313	0.059	0.029
9.273	1.340	4.410	34.510	42.046	41.910	0.136	0.053
5.311	2.010	4.723	38.649	43.897	43.614	0.283	0.125
5.740	3.358	4.955	42.019	45.495	45.127	0.368	0.189
5.992	6.071	5.250	46.701	47.251	47.681	0.430	0.277
4.535	7.083	5.553	51.650	49.902	49.449	0.453	0.371
3.248	9.523	5.981	59.816	53.656	53.114	0.541	0.525
1.996	12.045	6.404	68.795	57.630	57.144	0.486	0.695
0.814	12.961	6.601	77.540	61.963	61.560	0.403	0.858
0.427	14.270	6.910	81.045	62.952	62.642	0.310	0.927
b. Methanol(1)-2-Butanol (2) System:							
0.460	22.768	4.290	72.242	90.330	90.292	0.038	0.045
0.448	4.895	4.283	66.762	83.631	83.525	0.106	0.175
0.833	4.905	4.277	62.256	78.090	77.961	0.129	0.282
1.988	4.906	4.263	54.299	68.339	68.136	0.204	0.471
2.719	4.901	4.256	50.468	63.621	63.404	0.217	0.562
3.114	4.900	4.253	49.076	61.897	61.685	0.212	0.595
4.208	4.908	4.248	46.146	58.273	58.067	0.206	0.665
7.672	3.777	4.239	39.424	49.890	49.766	0.124	0.825
8.263	2.500	4.237	36.907	46.734	46.657	0.077	0.884
6.545	1.303	4.233	35.378	44.827	44.764	0.063	0.921

where W_1 = Weight of methanol in the mixture in gm.

W_2 = Weight of dichloromethane or 2-butanol in the mixture in gm.

W_3 = Weight of the equilibrium mixture in the pycnometer in gm.

AVM = Average molecular weight ·

V_{actual} = Actual molar volume of the mixture

V_{ideal} = Ideal molar volume of the mixture

v^E = Excess molar volume

Volume of the pycnometer = 5.365 cc

All volumes are expressed in cc/gm.mole

REFERENCES

1. Beattie, J.A., Chem.Rev., 44, 141 (1949).

2. Carlson, H.C., Colburn, A.P., Ind. Eng. Chem., 34, 581(1942).

3. Chhotray, S.K., M.Tech.Thesis, Department of Chemical Engineering, Indian Institute of Technology, Kanpur (1971).

4. Cox, J.D., Trans. Farad. Soc., 57, 1674 (1961).

5. Hala, E., Pick, J., Fried,V., Volliam, O., "Vapor Liquid Equilibrium," Pergamon Press, Oxford (1967).

6. Hala, E., Wichterle, I., Polak, J., Boublik, T. "Vapor Liquid Equilibrium Data at Normal Pressures", Pergamon Press, Oxford (1968).

7. Hill, W.D., Vanwinkle, M., Ind. Eng. Chem., 44, 205 (1952).

8. Hipkin, H., Myers, H.S., Ind. Eng. Chem., 46, 2524 (1954).

9. King, M.B., "Phase Equilibrium in Mixtures" Pergamon Press, Oxford (1969).

10. Kreglewiski, A., J. Phys. Chem., 608, 73 (1969).

11. Kudchadker, A.P., Ph.D. Thesis, Texas A&M University (1968).

12. Myers, H.S., Ind.Eng. Chem., 47, 2215 (1955).

13. Nagata, I., J. Chem.Eng. Data., 7(3), 367 (1962).

14. Orye, R.U., Prausnitz, J.M., Ind.Eng.Chem. 57(5), 18 (1965).

15. O'Connell, J.P., Prausnitz, J.M., I&EC (Process Design & Develop) 6, 245, (1967).

16. Prausnitz, J.M. "Molecular Thermodynamics of Fluid Phase Equilibria", Englewood Cliffs., N.J., Prentice Hall, Inc. (1967).

17. Prausnitz, J.M. Eckert, C.A., Orye, R.U., O'Connell, J.P., "Computer Calculations for Multicomponent Vapor Liquid Equilibria", Englewood Cliffs. N.J., Prentice Hall (1967).

18. Redlich, O., Kister, A.T., Ind. Eng. Chem., 40, 345 (1948).

19. Sarma, H., M.Tech. Thesis, Department of Chemical Engineering, Indian Institute of Technology, Kanpur (1970).

20. Scheller, W.A. Stanley, J.L. J. Chem. Eng. Data, 12(4)485(1967).

21. Tonn, F.G. Missen, R.W., Can. J. Chem. Eng. 41, 12-4(1963).

22. Timmermans, J., " Physico Chemical Constants of Pure Organic Compounds"; (Vols. I & II), Elsevier Publishing Inc., (1950, 1965).

23. Thomas, K.T., McAllister, R.A., A.I.Ch.E. Journal(3 161 (1957).

24. Vogel, A.I., "A Text Book of Practical Organic Chemistry including Qualitative Organic Analysis", p.169-70, (3rd Ed.) London, Longmans, Green (1959).

25. Selected Values of properties of Hydrocarbons and Related Compounds", American Petroleum Research Project 44, Thermodynamics Research Centre, Texas A&M University, College Station, Texas.

APPENDIX I

CALIBRATION OF CHROMEL-ALUMEL THERMOCOUPLE

In the present study chromel-alumel thermocouple
(temperature range:0° to 600°C) was chosen for temperature
measurement, though copper-constantin thermocouple (temperature
range -200° to 500°C) is preferred at low temperatures. It
was found that the hot junction of the latter is quite fragile
and easily susceptible to mechanical failures, which might
cause an error in the subsequent temperature measurements.

The calibration of thermocouple E.M.F. was done against a ~~25~~
25ohms platinum resistance thermometer (Leeds and Northrup
Company, S. No.17181311), the resistance of which is measured
upto four decimal places (corresponding to an accuracy of
± 0.005°C in temperature), with the help of a thermometer
bridge (8079-B, type ER, Leeds and Northrup Company) coupled
with a null detector (Leeds & Northrup Company, type -2430).
The resistance measured is directly related to the temperature
by the following relationship:

$$R_t = R_o \ (1 + \ \alpha t + \ \beta t^2)$$

where

R_t = Resistance at t°C

R_o = Resistance at 0°C

α = 0.003986   constants of the particular
                                    platinum resistance thermometer
β = -0.000001   used.

The E.M.F. of the thermocouple was measured using a Honeywell potentiometer, which can read upto three decimal places of voltage (corresponding to an accuracy of ± 0.02°C in temperature).

The thermocouple hot junction and the platinum resistance thermometer were immersed in a constant temperature bath (Made in Germany). The cold junction of the thermocouple was maintained at 0°C by immersing it in a flask containing a slurry of water and ice and sufficient care was taken to avoid air pockets. The lead wires from the cold junction (made of thick copper) were connected to the proper terminals of the potentiometer.

The bath mediums used were 1. water in the temperature range 35°–90°C and 2. Mauva oil in the temperature range 90°–115°C.

The bath medium was heated to the approximate required temperature and when steady state was attained, the E.M.F. and the resistance were noted. The calibration was done from 35°C to 115°C in the increments of 5°C (approximately) and the data are presented in Table A. The plot of temperature vs. E.M.F. is shown in Fig.14.
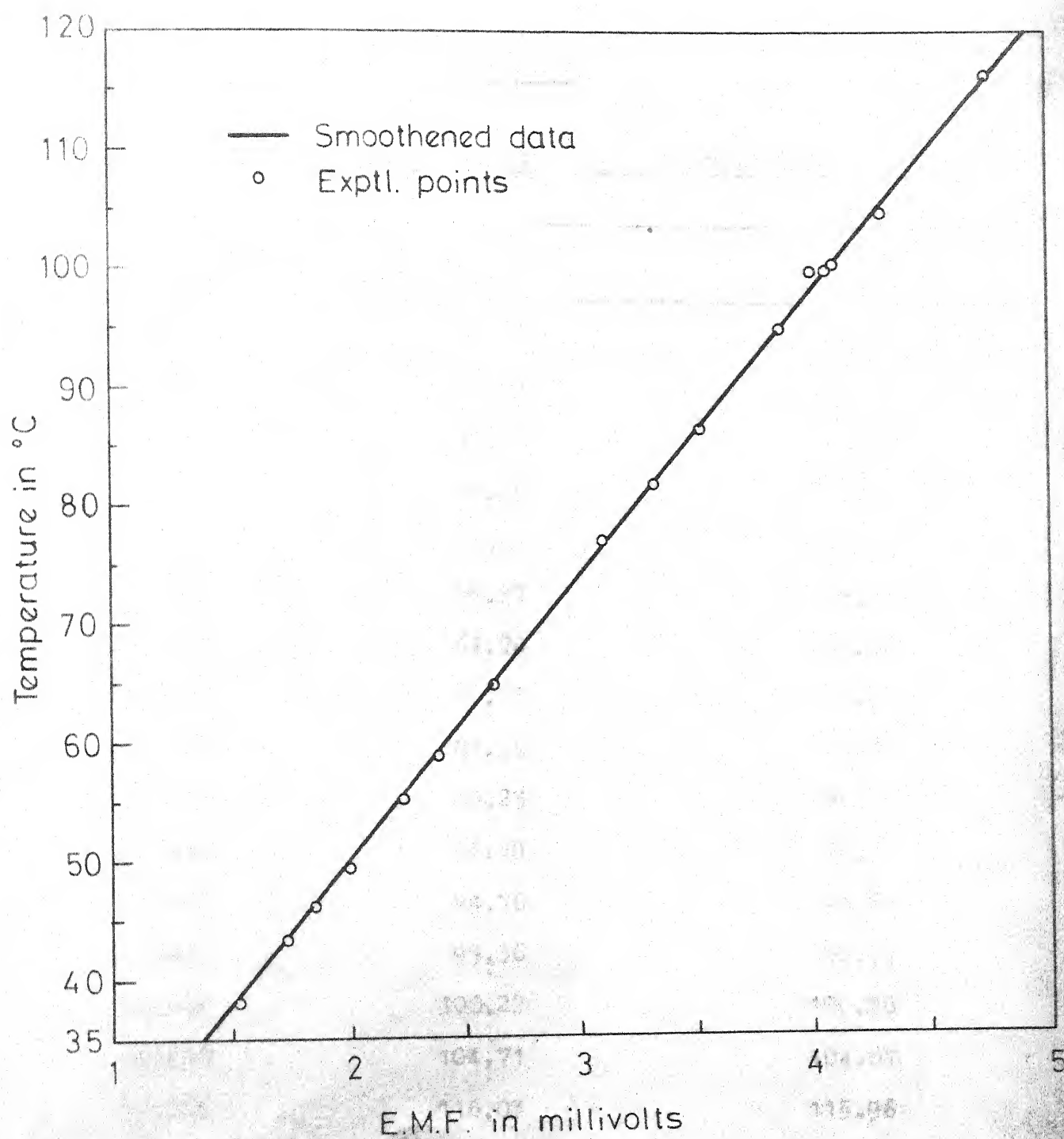
Fig.14 - Temperature E.M.F. diagram.

TABLE - A

CALIBRATION DATA FOR CHROMEL-ALUMEL THERMOCOUPLE

Thermocouple E.M.F. in m.V.	t,°C (measured value)	t,°C (smoothened value)
1.5280	38.16	38.30
1.7275	43.14	43.08
1.8320	45.55	45.58
1.9910	49.36	49.39
2.2360	55.23	55.26
2.3860	58.87	58.85
2.6270	64.70	64.62
3.0930	75.75	75.78
3.3250	81.55	81.34
3.5270	86.23	86.18
3.5450	86.70	86.61
3.8805	94.76	94.64
4.0910	99.56	99.69
4.1200	100.22	100.38
4.3015	104.71	104.87
4.7705	116.03	115.96

APPENDIX - II

CALIBRATION OF REFRACTOMETER

The analysis of equilibrium samples of liquid and vapor was carried out using a "Bausch & Lomb" precision refractometer (Type - Abbe-3L) as this method is quite fast and sufficiently accurate for our purpose.

Different compositions of the mixture were made using a clean dry sample tube of 5 ml capacity with the help of a Mettler balance (accuracy - 0.00001 gms), such that the whole compositions range was covered. The mole fractions of component one in the mixture was calculated as follows:

$$x_1 = \frac{W_1/M_1}{W_1/M_1 + W_2/M_2}$$

where

x_1 = mole fraction of component 1 in the binary mixture

W_1 = weight of the sample tube

W_2 = W_1 + weight of component 1

W_3 = W_2 + weight of component 2

M_1 and M_2 are the molecular weights of components 1 and 2 respectively.

Refractive index of each sample was measured by placing about 1 to 2 drops of the sample on the refractometer prism which was precalibrated. The temperature of the prism was kept throughout at $25 \pm 0.1^\circ C$. by circulating water through the prism with the help of a constant temperature bath.

In the case of dichloromethane-methanol system, the sample was kept in an ice flask until the refractive index was measured to minimize evaporation losses due to the presence of low boiling dichloromethane.

The refractive index - composition data thus obtained for the dichloromethane-methanol system and methanol-2-butanol system along with the smoothened data are presented in tables A and B respectively.

TABLE   A

CALIBRATION OF REFRACTOMETER FOR DICHLORO- METHANE(1) – METHANOL (2) SYSTEM

| x_1 | | |
Measured value	Smoothened value	R.I. (at $25 \pm 0.1°C$)
0.000	0.000	1.3268
0.039	0.036	1.3314
0.043	0.043	1.3325
0.060	0.061	1.3340
0.123	0.124	1.3433
0.211	0.208	1.3534
0.399	0.404	1.4743
0.519	0.508	1.3840
0.539	0.545	1.3873
0.548	0.549	1.3876
0.602	0.600	1.3920
0.769	0.767	1.4052
0.813	0.817	1.4089
0.848	0.848	1.4112
0.921	0.923	1.4145
0.949	0.946	1.4180
1.000	1.000	1.4212

TABLE – B

CALIBRATION OF REFRACTOMETER FOR METHANOL(1)
–2– BUTANOL (2) SYSTEM

x_1 Measured value	Smoothened Value	R.I. (at 25 $\pm$ 0.1°C)
0.000	0.000	1.3949
0.090	0.093	1.3919
0.131	0.120	1.3909
0.216	0.210	1.3875
0.280	0.288	1.3842
0.416	0.416	1.3782
0.430	0.429	1.3775
0.475	0.475	1.3751
0.499	0.498	1.3738
0.515	0.515	1.3728
0.640	0.643	1.3645
0.722	0.726	1.3580
0.734	0.731	1.3575
0.740	0.746	1.3562
0.777	0.783	1.3528
0.870	0.871	1.3434
0.882	0.879	1.3424
0.912	0.910	1.3387
0.965	0.963	1.3320
0.984	0.983	1.3294
1.000	1.000	1.3270

APPENDIX III

COMPARISON OF EXPERIMENTAL BOILING POINT, REFRACTIVE INDEX AND LIQUID DENSITY* WITH THE LITERATURE VALUES (25)

Substance	Experimental Values			Literature Values		
	$t°C$	η_D	d (gms/cm^2)	$t°C$	η_D	d (gms/cm^3)
Methanol	64.55	1.3270	0.7868	64.51	1.3266	0.7865
Dichloro-methane	39.75	1.4212	1.3170	39.75	1.4212	1.3163
2-Butanol	99.40	1.3949	0.8020	99.50	1.3949	0.8023

*Refractive index and liquid densities are reported at $25 \pm 0.1°C$

APPENDIX IV

PHYSICAL PROPERTIES (25) OF PURE COMPOUNDS

Substance	Antoine Constants			P_c (atm.)	V_c (lit/mole)	T_c (°K)	Z_c
	A	B	C				
Methanol	7.898	1474.08	229.13	79.9	0.118	512.58	0.224
Dichloro-methane	7.080	1138.91	231.45	60.0	–	510.00	–
2-Butanol	7.474	1314.19	186.55	41.39	0.268	536.01	0.252
Chloroform	6.995	904.25	243.60	65.90	0.143	416.20	0.267
Carbontetra-chloride	6.934	1242.43	230.00	44.97	0.275	556.30	0.271
Acetone	7.232	1277.03	237.23	46.60	0.229	508.70	0.256

APPENDIX V (a)

VIRIAL COEFFICIENTS*, FUGACITY COEFFICIENTS AND LIQUID MOLAR VOLUMES* FOR DICHLOROMETHANE (1)-METHANOL (2) SYSTEM (AT 760 mm MERCURY PRESSURE) AT THE REQUIRED TEMPERATURES

$t°C$	B_{11}	B_{22}	ϕ_1	ϕ_2	V_{L1}	V_{L2}
64.00	−585.0	−852.0	1.08	0.97	68.48	42.07
63.00	−589.0	−869.0	1.07	0.97	68.37	42.01
62.00	−593.0	−886.0	1.07	0.97	68.27	41.94
61.00	−598.0	−905.0	1.06	0.97	68.16	41.81
59.00	−605.0	−938.0	1.05	0.97	68.00	41.78
58.00	−613.0	−971.0	1.04	0.97	67.86	41.70
57.00	−619.0	−995.0	1.04	0.97	67.75	41.64
54.90	−634.0	−1050.0	1.03	0.98	67.53	41.52
51.67	−663.0	−1138.0	1.02	0.99	67.19	41.34
49.14	−692.0	−1207.0	1.01	0.99	66.92	41.20
46.98	−721.0	−1265.0	1.00	1.01	66.69	41.08
45.02	−753.0	−1317.0	0.99	1.02	66.48	40.99
43.23	−784.0	−1367.0	0.99	1.03	66.29	40.90
41.66	−814.0	−1412.0	0.98	1.04	66.12	40.83
40.38	−840.0	−1450.0	0.98	1.05	65.98	40.77
39.45	−860.0	−1480.0	0.98	1.05	66.88	40.72
38.85	−873.0	−1499.0	0.99	1.06	66.82	40.70
38.46	−882.0	−1512.0	0.97	1.06	66.78	40.68
37.99	−893.0	−1527.0	0.97	1.07	66.72	40.66
37.60	−919.0	−1564.0	0.97	1.08	66.60	40.61
37.40	−916.0	−1562.0	0.97	1.08	66.62	40.62
38.00	−892.0	−1527.0	0.97	1.10	66.72	40.66
38.19	−888.0	−1521.0	0.97	1.11	66.74	40.67
38.79	−875.0	−1501.0	0.97	1.12	66.81	40.69

*Virial coefficients and liquid molar volumes are expressed in units of cc/gm.mole.

APPENDIX V(b)

VIRIAL COEFFICIENTS*, FUGACITY COEFFICIENTS AND LIQUID MOLAR VOLUMES* FOR DICHLOROMETHANE (1)-METHANOL (2) SYSTEM (AT 750 mm MERCURY PRESSURE) AT THE REQUIRED TEMPERATURES

$t°C$	B_{11}	B_{22}	ϕ_1	ϕ_2	V_{L1}	V_{L2}
62.70	-593.0	-884.0	1.08	0.97	68.28	41.95
59.88	-603.0	-928.0	1.05	0.97	68.05	41.81
54.90	-634.0	-1050.0	1.03	0.98	67.53	41.52
50.92	-671.0	-1159.0	1.01	0.99	67.11	41.30
46.20	-734.0	-1286.0	1.00	1.01	66.61	41.05
42.00	-807.0	-1402.0	0.98	1.03	66.16	40.85
39.40	-861.0	-1481.0	0.98	1.05	65.58	40.73
37.82	-897.0	-1533.0	0.97	1.06	65.71	40.66
37.62	-902.0	-1540.0	0.97	1.07	65.68	40.65
37.38	-907.0	-1548.0	0.97	1.07	65.66	40.64
37.36	-908.0	-1549.0	0.97	1.07	65.66	40.64
37.36	-908.0	-1549.0	0.97	1.07	65.66	40.64
37.26	-910.0	-1552.0	0.97	1.07	65.65	40.63
37.18	-912.0	-1552.0	0.97	1.08	65.64	40.63
37.18	-912.0	-1555.0	0.97	1.08	65.64	40.63
37.20	-912.0	-1555.0	0.97	1.09	65.64	40.63
37.40	-905.0	-1545.0	0.97	1.10	65.67	40.64

*Virial coefficients and liquid molar volumes are expressed in units of cc/gm.mole

APPENDIX - V(C)

VIRIAL COEFFICIENTS*, FUGACITY COEFFICIENTS AND LIQUID MOLAR VOLUMES* FOR METHANOL (1)-CHLOROFORM (2) SYSTEM (AT 760 mm MERCURY PRESSURE) AT THE REQUIRED TEMPERATURES

$t\,^\circ C$	B_{11}	B_{22}	ϕ_1	ϕ_2	V_{L1}	V_{L2}
60.50	-915.0	-918.0	1.10	0.97	41.85	78.06
60.00	-925.0	-922.0	1.10	0.97	41.82	78.02
59.50	- 936.0	-926.0	1.09	0.97	41.79	77.97
59.00	-947.0	-931.0	1.09	0.97	41.76	77.93
57.90	-973.0	-941.0	1.08	0.97	41.69	77.83
56.30	-1013.0	-958.0	1.06	0.97	41.60	77.68
55.20	-1042.0	-970.0	1.05	0.97	41.53	77.58
54.40	-1063.0	-986.0	1.04	0.98	41.49	77.51
53.90	-1077.0	-986.0	1.04	0.98	41.46	77.47
53.70	-1083.0	-989.0	1.03	0.98	41.45	77.45
53.50	-1088.0	-991.0	1.03	0.98	41.44	77.43
53.55	-1088.0	-991.0	1.03	0.98	41.44	77.43
53.50	-1088.0	-991.0	1.02	0.98	41.44	77.43
53.70	-1083.0	-989.0	1-02	0.99	41.45	77.45
53.80	-1080.0	-987.0	1.02	0.99	41.45	77.46
54.00	-1074.0	-983.0	1.01	0.99	41.47	77.48
54.30	-1066.0	-981.0	1.01	0.99	41.48	77.50
54.70	-1055.0	-976.0	1.01	1C.00	41.54	77.59
55.30	-1039.0	-969.0	1.00	1.00	41.54	77.59
55.90	-1024.0	-962.0	1.00	1.01	41.59	7765
57.00	-995.0	-950.0	0.99	1.01	41.64	77.74
57.80	-976.0	-942.0	0.98	1.02	41.69	77.82
59.30	-905.0	-923.0	0.98	1.03	41.79	77.95
60.90	-907.0	-914.0		1.05	41.87	78.10
62.00	-886.0	-905.0	0.97	1.06	41.94	78.20
63.00	-869.0	-898.0	0.97	1.08	42.00	78.29

TABLE - V(d)

VIRIAL COEFFICIENTS*, FUGACITY COEFFICIENTS AND LIQUID MOLAR VOLUMES* OF METHANOL (1)-CARBON TETRA CHLORIDE SYSTEM (AT 760 mm MERCURY PRESSURE) AT THE REQUIRED TEMPERATURES

$t°C$	B_{11}	B_{22}	ϕ_1	ϕ_2	V_{L1}	V_{L2}
76.10	−729.0	−1051.0	1.10	0.96	42.90	103.62
75.85	−731.0	−1053.0	1.10	0.96	42.88	103.58
72.35	−758.0	−1086.0	1.08	0.96	42.63	103.07
67.60	−804.0	−1128.0	1.08	0.97	42.30	102.40
66.85	−813.0	−1135.0	1.05	0.97	42.25	102.30
62.00	−886.0	−1177.0	1.03	0.98	41.94	101.63
59.40	−938.0	−1209.0	1.01	0.99	41.78	101.27
57.20	−990.0	−1243.0	1.01	0.99	41.65	100.98
56.95	−996.0	−1247.0	1.01	1.00	41.64	100.95
56.25	−1014.0	−1258.0	1.00	1.00	41.59	100.85
55.80	−1026.0	−1265.0	1.00	1.00	41.57	100.79
55.75	−1027.0	−1266.0	1.00	1.00	41.57	100.79
55.75	−1027.0	−1266.0	1.00	1.00	41.57	100.79
55.70	−1029.0	−1267.0	1.00	1.00	41.56	100.78
55.65	−1030.0	−1267.0	1.00	1.01	41.56	100.78
55.70	−1029.0	−1267.0	1.00	1.01	41.56	100.78
55.70	−1029.0	−1267.0	1.00	1.01	41.56	100.78
55.70	−1029.0	−1267.0	1.00	1.01	41.56	100.78
55.75	−1027.0	−1266.0	0.90	1.01	41.57	100.79
55.75	−1027.0	−1266.0	0.99	1.01	41.57	100.79
56.00	−1021.0	−1262.0	0.99	1.01	41.58	100.82
56.00	−1021.0	−1262.0	0.99	1.01	41.58	100.82
56.35	−1012.0	−1257.0	0.99	1.02	41.60	100.87
56.75	−1002.0	−1251.0	0.99	1.02	41.62	100.92
57.10	−993.0	−1245.0	0.98	1.02	41.64	100.97
57.70	−978.0	−1235.0	0.98	1.03	41.68	101.05

Table V(d) continued

t°C	B_{11}	B_{22}	$\emptyset_1$	$\emptyset_2$	V_{L1}	V_{L2}
58.20	-966.0	-1227.0	0.99	1.03	41.71	101.11
58.60	-957.0	-1221.0	0.98	1.04	41.73	101.17
59.50	-936.0	-1208.0	0.98	1.05	41.79	101.29
60.40	-917.0	-1195.0	0.97	1.06	41.84	101.41
60.85	-908.0	-1189.0	0.97	1.06	41.87	101.47
61.80	-890.0	-1179.0	0.97	1.07	41.93	101.60
62.80	-872.0	-1169.0	0.97	1.09	41.99	101.74
63.50	-860.0	-1163.0	0.97	1.09	42.04	101.83
64.10	-851.0	-1158.0	0.97	1.09	42.08	101.91
64.50	-845.0	-1155.0	0.97	1.10	42.10	101.97
64.60	-843.0	-1154.0	0.97	1.11	42.11	101.98

*Virial coefficients and liquid molar volumes are
expressed in units of cc/gm.mole